

DEPARTMENT OF THE INTERIOR

FRANKLIN K. LANE, SECRETARY

BUREAU OF MINES

VAN. H. MANNING, DIRECTOR

THE FUSIBILITY OF COAL ASH AND  
THE DETERMINATION OF THE SOFTENING  
TEMPERATURE

BY

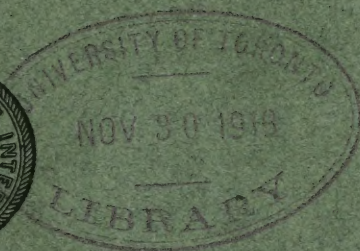
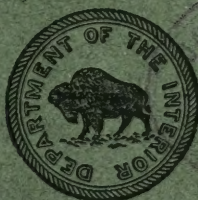
ARNO C. FIELDNER, ALBERT E. HALL

AND

ALEXANDER L. FEILD

ENGINEERING

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WASHINGTON  
GOVERNMENT PRINTING OFFICE  
1918



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# CONTENTS.

	Page.
Introduction .....	1
Purpose of investigation.....	1
Scope of investigation.....	1
Historical review .....	2
Eugene Prost, 1895 and 1897.....	2
Henry Le Chatelier, 1902.....	3
J. W. Cobb, 1904.....	3
E. G. Bailey and W. B. Calkins, 1910 and 1911.....	4
L. S. Marks, 1910.....	5
E. J. Constam, 1913.....	6
L. S. Marks, 1914.....	7
F. C. Hubley, 1914.....	9
O. W. Palmenberg, 1915.....	11
E. B. Ricketts, 1915.....	12
Composition of ash and distribution of ash-forming constituents in coal.....	13
Intrinsic ash .....	13
Extraneous ash .....	14
Nature of fusion of ash.....	15
Relation of melting points of ash constituents to fusion in the mixture .....	16
Formation of compounds and eutectics as illustrated in lime-silica system .....	17
Determination of the melting interval.....	18
Relation of melting interval to clinker formation.....	18
Determination of softening temperature.....	19
Factors influencing softening temperature.....	20
Influence of iron oxides.....	20
Experiments with Seger cones.....	22
Description of furnaces.....	22
Description and analyses of coal samples used in tests.....	25
Preparation of ash.....	29
Preparation of cones.....	29
General method of heating.....	30
Temperature measurements .....	30
Summary of results obtained in the different furnaces.....	32
Variations due to size and shape of cone.....	32
Influence of fineness of ash.....	33
Influence of inclination of cones.....	33
Influence of rate of heating.....	35
Influence of dextrin binder.....	36
Influence of various atmospheres.....	37
Appearance of cones softened in various atmospheres.....	42
Platinum furnace, atmosphere of air.....	42
Molybdenum furnace, atmosphere of hydrogen.....	43
Northrup furnace, atmosphere of carbon monoxide and nitrogen .....	43

	Page.
Standard methods for determining softening temperature of ash .....	44
Fusibility of coal ash in mixtures of hydrogen and water vapor .....	44
Theoretical consideration .....	44
Outline of experiments .....	46
Description of furnace .....	46
Description of "saturator" .....	48
Preparation of test piece .....	49
Measurement of temperature .....	49
Results of experiments .....	49
Fusibility of coal ash in mixtures of carbon monoxide and carbon dioxide .....	53
Theoretical considerations .....	53
Method of conducting experiments .....	54
Preparation of gas mixtures .....	55
Results of experiments .....	56
Discussion of results .....	62
Relation of softening temperatures in atmospheres of hydrogen and water vapor, and of carbon monoxide and carbon dioxide to clinker formation in furnaces .....	63
Ferrous, ferric, and metallic iron in fused ash cones and clinker slags .....	64
Relative merits of CO-CO <sub>2</sub> and H <sub>2</sub> -H <sub>2</sub> O atmospheres as standard atmospheres for fusion tests .....	67
Modified molybdenum furnace and saturator for softening-point determinations in H <sub>2</sub> -H <sub>2</sub> O atmosphere .....	74
Description of furnace and saturator .....	74
Experiments with vertical and horizontal placing of cones in determination of softening temperature .....	79
Method of conducting experiments .....	80
Results of experiments .....	81
Effect of dextrin binder or residual carbon on softening temperature of ash, and its relation to intumescence of softening cone .....	86
Swelling of melting ash cones .....	86
Experiments to determine effect of unburned carbon in ash on softening of cone .....	86
Molybdenum furnace as standard furnace for fusion tests .....	89
Fusibility of coal ash as determined in gas furnace .....	90
Theoretical considerations .....	90
Description of furnace .....	90
Method of operation .....	92
Composition of atmosphere surrounding cones .....	93
Testing for magnetic slag and metallic iron .....	95
Temperature measurements .....	95
Results of tests .....	96
Comparison of results obtained in two different types of gas furnaces operated under maximum reducing conditions .....	96
Comparison of results obtained with natural and with artificial gas .....	98
Ignition of ash in oxygen .....	101
Influence of size and shape of cone .....	102
Results of experiments .....	104
Influence of rate of heating .....	107
Determination of fluid temperature .....	108
Discussion of results obtained in gas furnace with reducing atmosphere .....	110



	Page.
Recommended procedure for standard gas-furnace method.....	111
Preparing the ash.....	111
Preparation of cones.....	111
Method of heating.....	112
Summary and conclusions.....	114
Acknowledgments.....	117
Bibliography.....	119
Fusibility and clinkering of coal.....	119
Contributions to the physical chemistry of slag and silicates.....	123
Melting and softening temperatures of oxides, sulphides, silicates, mixtures, and slags.....	130
Pyrometric cones; their use in measuring temperature.....	134
Pyrometers and the measurement of high temperature.....	135
Laboratory furnaces for high-temperature work.....	136
Publications on the utilization of coal and lignite.....	139
Publications available for free distribution.....	139
Publications that may be obtained only through the Superintendent of Documents.....	140
Index.....	142

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## TABLES.

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TABLE 1. Character and source of coal samples.....	26
2. Analyses of ash and coal.....	27
3. Results of tests showing influence of size of cone on softening temperature.....	32
4. Influence of fineness of ash on softening temperature.....	33
5. Influence of inclination of cones on softening temperature.....	33
6. Results of tests showing comparative softening temperatures in molybdenum furnace No. 2 at two different rates of heating.....	36
7. Results of experiments to determine influence of dextrin binder on softening temperature of ash cones.....	37
8. Results of tests to determine influence of various atmospheres on softening temperatures of ash cones in different furnaces.....	42
9. Results of experiments to determine softening temperatures of ash in various mixtures of hydrogen and water vapor.....	50
10. Results of tests to determine softening temperatures of certain ash samples in an atmosphere containing equal parts of CO and CO <sub>2</sub> .....	61
11. Results of tests to determine comparative effects on softening temperatures of ash of atmospheres of air, of water vapor, of carbon dioxide, of carbon monoxide, of equal parts of hy- drogen and water vapor, and of equal parts of carbon monox- ide and carbon dioxide.....	63
12. Results of analyses of ash cones fused in various atmospheres and of furnace clinkers.....	65
13. Results of tests to determine softening temperatures of coal ashes containing various percentages of ferric oxide in vari- ous atmospheres.....	68

	Page.
TABLE 14. Results of tests to determine softening temperatures of standard pyrometric cones in $H_2$ - $H_2O$ and $CO$ - $CO_2$ atmospheres, and in air-----	72
15. Results of softening-temperature tests, showing relative effects of vertical and horizontal placing of cones-----	82
16. Results of analyses of coal ashes and synthetic mixtures tested with the cones used in the vertical and in the horizontal position-----	82
17. Results of analyses of coal ashes used in experiments to determine influence of carbon on the softening temperature and the intumescence of ash cones-----	87
18. Results of tests to determine influence of carbon on the softening temperature and on the intumescence of ash cones-----	88
19. Results of analyses of gas samples taken at various temperatures from No. 3 melter's furnace-----	93
20. Composition of furnace atmosphere at various temperatures-----	94
21. Results of tests to determine softening temperatures in No. 3 melter's furnace and in modified Meker furnace-----	98
22. Results of tests to determine softening temperatures in No. 3 melter's furnace with four different sizes of cones-----	104
23. Results of tests to determine softening temperatures in No. 3 melter's furnace at four different rates of heating-----	107
24. Results of tests to determine initial-deformation, softening, and fluid temperatures of 12 samples of ashes in No. 3 melter's furnace-----	110

## ILLUSTRATIONS.

PLATE I. A, Typical forms of cones fused in air in the platinum furnace; B, Typical forms of cones fused in hydrogen in the molybdenum furnace; C, Typical forms of cones fused in carbon monoxide in the Northrup furnace-----	42
II. Arrangement of silica-tube furnace and accessories-----	46
III. A, Clinker No. 20452, from grate of Roney stoker; B, Typical forms of cones fused in the No. 3 melter's furnace-----	66
IV. A, Molybdenum furnace and saturator; B, No. 3 melter's furnace arranged for fusing tests-----	74
FIGURE 1. Concentration-temperature diagram for the lime-silica system-----	17
2. Sections through platinum-wire resistance furnace-----	22
3. Meker muffle furnace No. 29-----	22
4. Molybdenum furnace-----	23
5. Granular-carbon resistance furnace-----	24
6. Arrangement for softening temperature test in Northrup furnace-----	25
7. Brass cone mold-----	29
8. Appearance of ash cones at various stages of softening-----	31
9. Curves showing results of tests to determine influence of rate of heating on the softening temperature of ash cones in an atmosphere of hydrogen-----	34



	Page.
FIGURE 10. Curves showing results of tests to determine influence of rate of heating on the softening temperature of ash cones in an atmosphere of air-----	35
11. Curves showing results of tests to determine softening temperatures in Meker furnace, muffle furnace No. 2, and platinum furnace-----	38
12. Curves showing results of tests to determine softening temperatures in Northrup, carbon-resistance, and platinum furnaces-----	40
13. Curves showing results of tests to determine softening temperatures in Northrup, platinum, and molybdenum furnaces-----	41
14. Equilibrium diagram of the system $H_2$ , $H_2O$ , Fe, FeO, and $Fe_3O_4$ -----	46
15. Vertical longitudinal section through silica-tube furnace-----	46
16. Front elevation of silica-tube furnace and vertical section through saturator-----	47
17. Curves showing softening temperatures (final deformation points) of coal ash in various mixtures of hydrogen and water vapor-----	51
18. Curves showing initial deformation temperatures of coal ash in various mixtures of hydrogen and water vapor-----	52
19. Equilibrium diagram of the system CO, $CO_2$ , Fe, FeO, and $Fe_3O_4$ -----	54
20. Curves showing softening temperatures of ash sample 16 in mixtures of CO and $CO_2$ and of $H_2$ and $H_2O$ -----	57
21. Curves showing softening temperatures of ash sample 5 in mixtures of CO and $CO_2$ and of $H_2$ and $H_2O$ -----	58
22. Curves showing softening temperatures of ash sample 12 in mixtures of CO and $CO_2$ and of $H_2$ and $H_2O$ -----	59
23. Curves showing softening temperatures of ash sample 9 in mixtures of CO and $CO_2$ and of $H_2$ and $H_2O$ -----	60
24. Curves showing softening temperatures of coal ash in gas furnace No. 3, in atmospheres of equal parts of $H_2$ and $H_2O$ , and of equal parts of CO and $CO_2$ , and in air, with special reference to the percentage of $Fe_2O_3$ in the ash-----	70
25. Curves showing initial deformation points of coal ash in gas furnace No. 3, in atmospheres of equal parts of $H_2$ and $H_2O$ , equal parts of CO and $CO_2$ , and in air, with special reference to the percentage of $Fe_2O_3$ in the ash-----	71
26. Vertical longitudinal section through molybdenum furnace No. 3-----	75
27. Front elevation of molybdenum furnace No. 3 and vertical section through saturator-----	76
28. Appearance of vertical and horizontal ash cones at various stages of softening-----	83
29. Appearance of vertical and horizontal ash cones at various stages of softening-----	84
30. Appearance of vertical and horizontal ash cones at various stages of softening-----	85
31. Section of No. 3 melter's furnace arranged for fusion tests----	91
32. Electromagnet used to determine magnetic properties of fused cones-----	95

	Page.
FIGURE 33. Modified No. 29 Meker furnace.....	97
34. Curves showing softening temperatures determined in No. 3 gas furnace and in modified No. 29 Meker furnace.....	99
35. Electric furnace for igniting ash in atmosphere of oxygen.....	102
36. Curves showing softening temperatures obtained in No. 3 melter's furnace with four different sizes of cones.....	105
37. Curves showing softening temperatures obtained in No. 3 melter's furnace at four different rates of heating.....	106
38. Curves showing temperatures of initial deformation and softening and fluid temperatures of 12 ashes in No. 3 melter's furnace.....	108



# THE FUSIBILITY OF COAL ASH AND THE DETERMINATION OF THE SOFTENING TEMPERATURE.

By ARNO C. FIELDNER, ALBERT E. HALL, and ALEXANDER L. FEILD.

## INTRODUCTION.

### PURPOSE OF INVESTIGATION.

As a safeguard against excessive clinker troubles, specifications for the purchase of coal can be drawn to include the "softening" or "fusing" temperature of the ash. The value of such information has been recognized by the Bureau of Mines and has induced the bureau to investigate laboratory methods of determining the fusibility of coal ash, and the bearing of the results on clinker formation in fuel beds. The bureau realized that the fusibility of a mixture of oxides and silicates such as is comprised in coal ash varies according to the conditions under which tests are made, and that in the absence of any generally accepted method, no agreement is to be expected among tests made in different laboratories. Indeed, Marks<sup>a</sup> has recently called attention to differences as great as 390° C. that were obtained with the same sample of ash by two different laboratories. Therefore if a fusion-temperature clause is to have any place in specifications for coal, a standard method of testing should be adopted in order to insure comparable results by different laboratories and to obtain the softening or fusing temperature of the ash under conditions similar to those of a fuel bed. After a consistent method has been devised for obtaining comparable results at different laboratories, there will remain the correlation of these results with those from the burning of coal in furnaces before the value of fusibility tests in coal specifications can be finally determined.

### SCOPE OF INVESTIGATION.

The present publication reviews the literature on the subject and gives in detail the effect of various oxidizing, reducing, and neutral

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<sup>a</sup> Marks, L. S., *The clinkering of coal*: Power, vol. 40, 1914, pp. 932-934.

atmospheres such as are found in various parts of the fuel bed on the softening temperature of ash when molded in the form of Seger cones. As a result of this study a practical method of determining fusibility has been developed whereby the ash is caused to soften and form slags in which the iron exists in approximately the same state of oxidation as the iron in fuel-bed clinkers.

Although it is believed that this method will indicate the probable clinkering characteristics of a coal better than any fusion tests heretofore described, the bureau does not recommend the general use of this method in coal specifications until it is justified by actual trial in furnace tests of different coals. As no fusibility test of a well-mixed sample of the average ash of a coal takes into account the physical distribution of the impurities in the coal as burned, much additional investigation is needed to establish the exact relation of these laboratory fusibility tests to clinker formation. In order to correlate this proposed test of minimum softening temperature with clinker formation, the bureau is now making clinkering tests in a specially designed experimental furnace, in which different coals having ashes that differ in fusibility are burned under similar and known conditions of combustion. The results of this investigation will be published in a subsequent report. In the meantime it is hoped that other investigators will obtain similar correlation data.

## HISTORICAL REVIEW.

### EUGENE PROST, 1895 AND 1897.

Prost<sup>a</sup> analyzed the ash and determined the temperature of fusion of 23 different types of Belgian coals. The fusion tests were made by placing 3 grams of finely pulverized ash in a small porcelain crucible and then heating it for definite periods of time at four different temperatures, namely, 1,100°, 1,250°, 1,400°, and 1,500° C. The temperatures were controlled by using gold and platinum alloys of known melting points. After each period of heating the ash was examined. The progress of fusion was described as "barely fritted," "fritted," "strongly fritted," "incipient fusion," or "fused."

To obtain the different temperatures Prost used three different furnaces, as follows: (1) A Perrot gas furnace which gave a maximum temperature of 1,100° C.; (2) a coke furnace which gave a maxi-

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<sup>a</sup> Prost, Eugene, *Récherches sur les relations existant entre le degré de fusibilité et la composition des cendres de houille*: *Rev. Univ. Min.*, t. 31, 1895, pp. 87-98; *Monit. Sci.*, t. 46, 1895, pp. 560-565; *Sur les relations entre la composition et la fusibilité des cendres de houille*: *Bull. Assoc. Belge chim.*, t. 11, 1897, pp. 119-126; *The fusibility and composition of coal cinders*: *Coll. Guard.*, vol. 70, 1895, p. 796; *The relation between composition and fusibility in coal ash*: *Coll. Guard.*, vol. 74, 1897, p. 602; *Fusibility of coal ash determined by its composition*: *Coll. Guard.*, vol. 75, 1898, p. 473.



mum temperature of 1,250° or 1,400° C., according to the method of operation; (3) a small blast furnace of fire brick which gave a maximum temperature of 1,500° C.

In furnaces 2 and 3 the crucibles containing the ash samples and the alloy-temperature indicators were placed in a fire-clay crucible with a wall 1 cm. thick. Coke was packed around this crucible. Prost calculated from the chemical analysis the refractory quotient:

$$Q = \frac{\begin{array}{c} \text{O in } \text{Al}_2\text{O}_3 \\ \text{O in CaO} + \text{O in } \text{Fe}_2\text{O}_3 + \text{O in MgO} \\ \text{O in } \text{SiO}_2 \\ \text{O in } \text{Al}_2\text{O}_3 \end{array}}$$

for 23 Belgian coal ashes; he found that in general the fusing temperature increased with the value of  $Q$ . There were, however, several exceptions to the calculated results, especially for ash of high iron content. Prost's method of determining relative fusibility was merely approximate; for the conditions of reduction or oxidation undoubtedly varied in his different furnaces. Also his estimate of the degree of fusion on mere observation of the appearance of the melt in a crucible would necessarily be rather indefinite, for judgment of different observers would vary.

#### HENRY LE CHATELIER, 1902.

Le Chatelier<sup>a</sup> used the Seger-cone method for determining the relative fusibility of different coal ashes. He burned the coal in a muffle at a low temperature, ground the ash fine, and then, using starch as binder, molded the ash into triangular pyramids 50 mm. (2 inches) high and 15 mm. ( $\frac{9}{16}$  inch) wide at the base. These pyramids were ignited to destroy the organic binder, placed in a gas furnace, with a suitable number of Seger pyrometric cones, and slowly heated until they collapsed. The temperature at which the vertex of a pyramid became half the original height of the cone was taken as the softening temperature. Le Chatelier gives no data on the possibility of reducing gases from the furnace atmosphere acting on the iron oxide of the ash.

#### J. W. COBB, 1904.

Cobb<sup>b</sup> ground coal ash to pass a 100-mesh sieve or to an impalpable powder, and, using dextrin solution for binder, made the ash into four-sided pyramids 3 inches (76 mm.) high and 1 inch (25 mm.) square at the base. Each pyramid was mounted with one face ver-

<sup>a</sup> Le Chatelier, Henry, Étude sur la fusibilité des cendre des combustibles: Bull. Soc. L'Ind. Nat., t. 102, 1902, pp. 223-229. Abstract (Fusibility of the ashes of fuels) in Jour. Soc. Chem. Ind., vol. 21, 1902, p. 459.

<sup>b</sup> Cobb, J. W., Coal ash: Jour. Soc. Chem. Ind., vol. 23, 1904, pp. 11-13.

tical, and placed in a circular, down-draft, regenerative furnace, heated by eight burners on the periphery.

Temperature measurements were taken with Seger pyrometric cones and with a thermocouple. The temperature of the furnace was raised slowly until the tips of the cones started to bend. The rate of heating was then checked to almost zero to allow the cones to bend slowly through a small range of temperature. Cobb gives no exact figures for rate of heating, but calls attention to the necessity of a uniform rate to insure comparable results, and also states that an oxidizing atmosphere must be maintained in the space surrounding the cones.

**E. G. BAILEY AND W. B. CALKINS, 1910 AND 1911.**

In 1910 Bailey and Calkins<sup>a</sup> published a paper giving experimental data on the relation between the fusing temperature of ash and the formation of clinker. Tests were made in two hand-fired furnaces with several coals having ash of different fusing temperatures. All clinkers larger than about 1 inch were picked out of the refuse and the ratio of clinkers to the total ash in the coal burned was determined. The results, plotted in curves, showed a rapid increase in the ratio of ash fused to clinkers as the fusing temperature fell below 1,371° C. (2,500° F.). The clinker made from a lower fusing ash obstructed more grate area than the same weight of clinker formed from an ash of higher fusing temperature.

In a subsequent paper Bailey<sup>b</sup> describes two 24-hour boiler tests with two coals A and B. The fusing temperatures of the ashes of these coals were 1,510° C. (2,750° F.) and 1,310° C. (2,390° F.). On the basis of the total ash in the coal, coal A formed 20.2 per cent and coal B 53.3 per cent of clinker. Also, the clinker from coal B was much more troublesome in that the clinkers were thinner, thus obstructing about one-third more grate area than the same weight of clinker from coal A. In several boiler tests of coals, made by Prof. E. A. Hitchcock at the Ohio State University, two coals, C and D, having ash that fused at 1,260° C. (2,300° F.) and at 1,450° C. (2,640° F.), were burned on a plain grate of 50 per cent air space, under a Dutch oven. The ash with the lower fusing temperature had a greater proportion fused to clinker than did the ash with the higher fusing temperature; also the clinker from coal C was thin and vitreous, thus offering more obstruction to the passage of air through the fuel bed than the fragile and porous clinker resulting from coal D.

<sup>a</sup> Bailey, E. G., and Calkins, W. B. Fusing temperatures of coal ash: Power, vol. 32, 1910, pp. 1978-1979, Fuel Testing Co. Bull. 5, 1911, 15 pp.

<sup>b</sup> Bailey, E. G., The fusing temperature of coal ash: Power, vol. 34, 1911, pp. 802-806; 1910, pp. 1978-1979.



Coals E and F, having ash that fused at  $1,210^{\circ}$  C. ( $2,210^{\circ}$  F.) and  $1,400^{\circ}$  C. ( $2,550^{\circ}$  F.), were burned on shaking grates under a fire-brick arch of a special horizontal return tubular boiler setting. These two coals did not show the difference in clinker formation that was expected from the difference in the fusing temperatures of the ashes. This result is ascribed to a probable difference in fuel-bed conditions and a difference in the burning characteristics of the two coals. However, the lower fusing ash from coal E formed a thinner clinker than coal F, obstructing approximately 0.21 square foot of grate area per pound, as compared to 0.13 square foot for the clinker from coal F.

Bailey concludes that the "main factor in the formation of clinker is the difference between the fusing temperature of the ash and the temperature to which it is subjected. Any factor, such as excess air, rate of combustion, and thickness of fuel bed which will affect the temperature may cause a corresponding change in the amount and nature of the clinker from a given coal."

#### L. S. MARKS, 1910.

Marks<sup>a</sup> used the Seger-cone method for determining the effect on the fusibility of ash of adding various proportions of  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{FeS}_2$ ,  $\text{Fe}$ ,  $\text{CaS}_2$ , and  $\text{CaSO}_4$ . The finely ground mixtures were molded into pyramids similar in shape and size to standard pyrometric cones, then mounted in a vertical position and slowly heated in a gas muffle. The temperatures were measured with a thermocouple. Sketches were made of the cones as they melted, and the corresponding temperatures were noted. The viscosity of the softening material was judged from the rapidity and manner of deformation of the cone. Certain mixtures melted to a fluid of the viscosity of water, others formed a spongy, viscous mass. Marks obtained the following results on adding various substances to the ash of a non-clinkering West Virginia coal, which had a softening temperature of  $1,400^{\circ}$  C. ( $2,550^{\circ}$  F.):

*Results of tests by Marks with the ash of a nonclinkering West Virginia coal in a gas muffle.*

Substance added.	Effect on softening temperature of ash of adding—			Fluidity of melt.
	25 per cent.	50 per cent.	75 per cent.	
$\text{Al}_2\text{O}_3$ .....	Raised.....	Raised.....	Raised.....	Very fluid.
$\text{CaO}$ .....	Lowered considerably.	.....	.....	
$\text{Fe}_2\text{O}_3$ .....	Lowered slightly.	Lowered slightly.	Lowered slightly.	Viscous.
$\text{FeS}_2$ .....	Lowered considerably.	Lowered considerably.	Lowered considerably.	
$\text{Fe}$ .....	.....do.....	Lowered somewhat.	Lowered slightly.	Very fluid.
$\text{CaS}_2$ .....	Lowered.....	Lowered considerably.	Lowered considerably.	
$\text{CaSO}_4$ .....	.....do.....	.....do.....	.....do.....	Do.

<sup>a</sup> Marks, L. S., The clinkering of coal; results of tests for effect of various constituents in the coal: Eng. News, vol. 64, 1910, pp. 623-626.

Similar clinkering tests were then made in a specially designed furnace, analogous results being obtained. Substances that lowered the softening temperature of the ash tended to increase the clinker formation. The addition of 3 per cent of pyrite ( $\text{FeS}_2$ ) to a non-clinkering West Virginia coal containing 6 per cent ash produced a hard, heavy clinker, which had a strong tendency to stick to the grate bars, thus choking the draft. Adding 2.2 per cent of ferrous sulphide ( $\text{FeS}$ ) caused a similar degree of clinker formation. The addition of 4.4 per cent of ferrous sulphide made a very fusible and extremely troublesome clinker, which flowed over and "froze" to the grate bars, seriously checking the draft. Addition of iron oxide with an iron content equivalent to that in the 3 per cent pyrite produced a somewhat less troublesome clinker than did the pyrite.

The tests seemed to indicate that, other things being equal, the sulphides of iron are more troublesome than the oxides.

#### E. J. CONSTAM, 1913.

Constam,<sup>a</sup> in 1913, reported the "melting temperatures" of the ash from 200 different samples of coal and coke from various European mines. His criterion of melting temperature was the deformation or softening point of the ash when molded in the form of a small pyramid. The pyramids were heated in a carbon-tube electric furnace having a magnesia tube closed at one end, in which the ash pyramid was placed. The temperatures of incipient softening, intumescing, and complete fusion were measured with a Holborn-Kurlbaum optical pyrometer. Constam gives no information on the rate of heating, exact size and shape of the test piece, or the character of the atmosphere in which it was heated, in his published report. At the temperatures necessary to fuse coal ash the magnesia tube would not protect the ash from the reducing action of the carbon monoxide evolved from the heating element, unless a vigorous current of air was circulated through the interior of the tube. In the absence of complete information as to whether oxidizing or reducing atmospheres were used in the fusion tests, Constam's results can not be properly classified, but they gave excellent agreement of the softening temperatures reported for different samples of coal from the same source, and for samples of ash from a given coal and from its resulting coke.

As a result of his investigations, Constam concludes that (1) the proportion of ash does not influence the softening temperature;<sup>b</sup> (2) the softening temperature is characteristic of the seam; (3) the

<sup>a</sup> Constam, E. J., Ueber Schmelztemperaturen von Kohlenaschen: Ztschr. Ver. Gas- und Wasserfachmänner in Oesterreich-Ungarn, Oct. 15, 1913. Abstract in Jour. Gas Lighting, vol. 124, 1913, p. 522.

<sup>b</sup> This conclusion does not hold when the ash contains an excess of a single constituent, as pyrite or slate.



softening temperature is not affected by coking the coal or by the temperature of coking; (4) the softening temperatures of different ashes ranged from  $1,150^{\circ}$  to  $1,700^{\circ}$  C.

Regarding various fuels, he recommends temperatures above which the ash of each fuel should fuse, as follows: Coke for a central heating plant,  $1,300^{\circ}$  C.; anthracite for the same purpose,  $1,400^{\circ}$  C.; coal for use under boilers,  $1,400^{\circ}$  C.; coal for locomotives,  $1,500^{\circ}$  C.; and coal for gas producers, about  $1,500^{\circ}$  C., or below  $1,200^{\circ}$  C.

#### L. S. MARKS, 1914.

Following the publication of Bailey's papers in 1910 and 1911, the growing demand for the fusibility test in connection with the purchase of coal under specifications led to the development of such tests in different laboratories. Although most of these tests depended on some modification of the well-known Seger-cone method used by Le Chatelier and by Cobb, highly discordant results were obtained by different laboratories with samples of the same ash. In 1914, Marks<sup>a</sup> called attention to differences as high as  $390^{\circ}$  C. in the fusing temperatures reported by different testing laboratories for samples of the same ash. An investigation of the causes of these variations led to the conclusion that the most important factor was the atmosphere surrounding the ash. Using the Seger-cone method, Marks determined the softening temperatures of 11 samples of ash in a Hoskins carbon resistance furnace and in a Meker muffle furnace; for each sample the Hoskins furnace gave the higher softening points, the difference ranging from  $120^{\circ}$  to  $255^{\circ}$  C. This variation in fusibility was attributed to the Hoskins furnace containing a reducing atmosphere of carbon monoxide and the Meker furnace having an oxidizing atmosphere from the air circulating through the muffle. Marks considers it essential that fusion tests be made in an oxidizing atmosphere.<sup>b</sup>

As less important causes for variations in the results of Seger-cone tests, Marks enumerates the following: (a) Size of cone; (b) position of cone; (c) nature of binder; (d) rate of heating; (e) location of cone in furnace; (f) material on which the cone is supported; (g) unburned carbon in the ash.

The use of a 10 per cent dextrin solution for binder and slight variations in the size of the cone had no appreciable effect on the results.

<sup>a</sup> Marks, L. S., The clinkering of coal: Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 205-208; Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 801-834.

<sup>b</sup> Combustion tests made for the Bureau of Mines by Henry Kreisinger, engineer, have shown that at ordinary rates of combustion almost all the oxygen in fuel-bed gases has disappeared at 3 inches above the grate bars, the gases at this point containing approximately 15 per cent  $\text{CO}_2$  and 14 per cent  $\text{CO}$ , the remainder being nitrogen and other combustible gases. It is therefore highly probable that clinker forms in a slightly reducing atmosphere, and that fusion tests of coal ash in air do not parallel furnace conditions.

The deformation temperatures of 11 different samples of ash tested in horizontally mounted<sup>a</sup> cones were from 5° to 50° C. lower than when similar samples were tested in vertically mounted cones. The average difference was 21° C. The smaller differences were observed with samples showing the greatest fluidity. Cones mounted horizontally were more sensitive to heat than those mounted in the usual manner, and gave indication that could be duplicated more closely.

Comparative tests of the effect of rate of heating with two samples of ash showed deformation points 40° and 35° C. lower at 6° increase per minute than at 2° per minute. This difference was ascribed to the increased lag of the thermocouple and its protecting porcelain tube at the higher rate of heating.<sup>b</sup>

Unburned carbon in the ash tended to increase the softening temperature.

Marks finally adopted as the most satisfactory modification of the Seger-cone method the molding of the ash into a cone 11 by 52 mm. ( $\frac{7}{16}$  inch by 2 inches), placed in a horizontal position on a quartz plate, with the apex projecting over the side of the support. The quartz plate was blocked up near the center of the muffle of a No. 29 Meker furnace. A stream of air provided an oxidizing atmosphere. A thermocouple, protected with a porcelain tube, was inserted through a hole in the back of the furnace, the cone being placed as near it as possible. The furnace was heated rapidly to within about 200° C. of the expected fusing temperature; the rate of temperature increase was then reduced to 2° C. per minute. The temperature of initial and of final bending (apex of the cone pointing vertically downward) was noted, and also the final appearance of the cone—whether it showed a fluid constituent that ran down and formed a knob on the vertex of the cone. This seemed to be somewhat characteristic of clinkering coals.

The results of tests in which the method of determining fusibility, described above was used, were compared with the clinkering results observed when 10 different coals were burned under normal power-house conditions. Marks, concludes that "a general relation was shown between the two, but not definite enough to be reliable. For the particular boiler plant investigated, it would seem that an ash

<sup>a</sup> As recommended by J. P. Sparrow of the New York Edison Co.

<sup>b</sup> Higher rates of heating should give higher softening temperatures owing to the time lag in the slag-forming reactions. This relation has been shown in experiments with Seger pyrometric cones by numerous investigators. See Zimmer, W. H., Practical experience with pyrometers: Trans. Am. Cer. Soc., vol. 1, 1899, pp. 23-38; Geijsbeck, S., The fusing points of Seger cones expressed in degrees: Trans. Am. Cer. Soc., vol. 6, 1904, pp. 94-99; Geijsbeck, S., The melting points of pyrometric cones under various conditions: Trans. Am. Cer. Soc., vol. 14, 1912, p. 849; Hoffman, G., Prüfung der Segerkegel: Sprechsaal, Bd. 44, 1911, pp. 143-145; Reike, R., Die Schmelzpunkte der Segerkegel 022-15; Sprechsaal, Bd. 44, 1911, pp. 726-728; Brown, G. H. and Murray, G. A., The function of time in the vitrification of clays: U. S. Bur. Standards Tech. Paper 17, 1913, p. 23.



with a fusing temperature (final bending) below  $1,400^{\circ}$  C. will probably give trouble if the ash cone shows a fusible constituent; whereas it will not give trouble with a fusing temperature above  $1,380^{\circ}$  C. if the ash is viscous. This conclusion would require further investigation with many other coals before it could be accepted even for this particular plant: naturally it can not be applied to plants with different operating conditions."

F. C. HUBLEY, 1914.

Various commercial laboratories that have developed individual modifications of the fusibility test seem to find a somewhat definite relation between the indications of their particular laboratory test and the clinkering characteristics of the fuel used in the power plants under their observation. Hubley,<sup>a</sup> after two years' experience with the Seger-cone method, considers it of value in predetermining the clinkering properties of a coal, and states that in most instances the clinkering of a coal in the boiler furnace agreed closely with the results of the laboratory tests.

Hubley used cones 2 inches high and 1 inch in diameter at the base. He ground the ash to pass a 60-mesh sieve; mixed it with 10 per cent by weight of dry dextrin and water enough to make a plastic mass, which was pressed in wooden molds, dried, and heated in a vertical position in a cylindrical Fletcher crucible furnace. Illuminating gas was used for heating to temperatures up to  $2,700^{\circ}$  F., and Blau gas for temperatures to  $3,000^{\circ}$  F. The temperatures were measured with a thermocouple, having the bare hot junction close to the cone. The temperature was gradually increased until signs of fusing appeared, as when the sides began to lose their sharp outlines, or when the body of the cone began to swell. The furnace was held at this temperature for three minutes, and then allowed to cool. Other cones from the same ash sample were in turn tested, the final temperatures for the lot being regulated to give a series at  $25^{\circ}$  or  $50^{\circ}$  F. intervals on either side of the temperature obtained in the preliminary test. Enough cones were tested to indicate a series from a temperature of no deformation to one at which the ash flowed readily. From this series the progress of fusion at various temperatures was determined.

This method gave satisfactory indication of probable clinkering characteristics, but proved tedious and somewhat lacking in definiteness, as the judgment of the operator entered too largely into the results.

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<sup>a</sup> Hubley, F. C., Bituminous coals; predetermination of their clinkering action by laboratory tests: Proc. Eng. Club of Philadelphia, vol. 32, January, 1915, pp. 35-85; abstracted in Power, vol. 40, 1914, p. 796; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 208-211; Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 815-824.

To remedy these objections, Hubley devised an apparatus, which he called a "fusiometer," for indicating mechanically the progressive softening of a pellet of ash. This apparatus consists of an iron frame carrying a small gas-fired furnace, into which project two carbon rods, one-half inch in diameter on a common vertical axis. Between the carbon rods is placed the ash sample, compressed without binder, under a pressure of 30,000 pounds per square inch, into the form of a cylindrical pellet five-eighths of an inch in diameter and one-half inch high. The upper carbon rod, free to move vertically between suitable guides, is weighted to exert a pressure on the ash pellet of 1.5 pounds per square inch. A silk cord connecting the upper end of the rod and a counterweight runs over a pivoted pulley to which is attached a pointer magnifying twelve times on a scale any expansion or contraction of the pellet. The temperature of the furnace is measured with a thermocouple. Temperatures up to 2,700° F. may be attained with illuminating gas, and above 3,000° F. with Blau gas.

The method of making a test is described by Hubley as follows:

The ash pellet is placed in position between the carbons and adjusted so that the pointer is midway between 0 and 1.00 on the scale. The furnace is then gradually heated at the rate of 50° to 100° F. per minute, simultaneous temperature and scale readings being made at  $\frac{1}{2}$ -minute intervals. As the heat is increased, negative movement of the pointer will indicate carbon expansion up to a temperature where first softening of the ash pellet is indicated by a positive movement of the pointer. The experiment is continued till final collapse of the pellet is indicated on the scale. These results, if plotted, the temperatures as abscissæ, and the pointer movement as ordinates, produce a curve, an ordinate of which at any point is a measure of the relative rate of softening of the ash pellet at that temperature.

The length of the softening range, and its position on the temperature scale in relation to the working temperature range of a boiler fire, as well as the increasing rate of softening, whether gradual throughout the range (indicating high viscosity), or very slight for most of the range, followed by a sudden collapse, are the factors in the fusiometer results which must be considered in predicting the probable clinkering action of a coal in a boiler fire. A long range ash with a slow but steady increase in softness, apparently indicated by the gently sloping curve, is productive of the close gummy clinker of high viscosity. This type, provided the softening range coincides approximately with the working temperature range of the boiler, produces the greatest losses from clinker formation in a boiler fire. This refers more particularly to stokers in which the fires are cleaned at regular intervals by a dropping of the back grates.

The other type of ash fusion is a short-range, spongy, porous formation of low viscosity, which, if it does not occur too low on the temperature scale, can be handled with ease in the boiler fires. From a comparison of boiler-house results with a large number of tests made, the fusiometer curve for this type of fusion appears to be distinguished by a most decided downward dip in the curve just prior to final softening.

The term "fusing point" is misleading and indeterminate, while "fusing range" of a substance can be determined with exactitude. For purposes of



relative comparison, however, an arbitrary point in the fusing range may be selected and called the "fusing point" of the ash. For this point in the case of the fusiometer results, the author suggests the temperature at which the pellet has collapsed, owing to softening, to one-half of its original height.

Hubley shows a number of fusiometer curves illustrating the two types of fusion and discusses them together with the boiler-house reports in regard to the nature and extent of clinker formed under actual operating conditions. He states that usually he found these curves of much use in indicating the clinkering characteristics of the coals represented, and suggests the following specification:

The pellet shall not have collapsed due to softening to more than one-half of the original height at a temperature,  $T$ , and in addition shall not show a collapse of more than one-eighth of the original height due to softening at a temperature of  $300^{\circ}$  F. under temperature  $T$ .

The first part of this specification will limit the final fusion, while the second part is intended to control viscosity and avoid a sloping curve. The fixing of temperature  $T$  must vary with plant conditions. It is obvious that the buying field for steam coal will be restricted or broadened according as the temperature  $T$  is raised or lowered, so that the fixing of this temperature must be governed by the value which a plant management places on a loss of boiler capacity, and risk of steam failure against the saving made in purchasing the cheaper fuel.

The excellent agreement Hubley obtained on duplicate samples of the same ash does not prove that the method will give correspondingly close agreement in different laboratories, as variations in the slagging reactions of the ash will affect results obtained by this method as well as those obtained by the Seger-cone method. The principal factors would be the nature of the atmosphere—whether oxidizing or reducing—and the rate of heating. If a gas furnace is used, the nature of the atmosphere will vary with different adjustments of gas to air. The effect of different atmospheres on the softening of cones is described elsewhere. Undoubtedly their effect will be similar in the fusiometer furnace.

#### O. W. PALMENBERG, 1915.

Palmenberg<sup>a</sup> states that the Seger-cone method, modified as described below, is used in his laboratory, and has proved satisfactory in furnishing laboratory results that are comparable with the results obtained in practice.

The coal ash which has been burned free of carbon and heated to insure oxidation of the iron is made into a round, thin cone  $1\frac{1}{2}$  to 2 inches high, weighing about 1 gram or less. This cone is placed upon a thin piece of Battersea fire clay in a vertical position and set in the middle of the muffle of a Meker

<sup>a</sup> Palmenberg, O. W., Discussion of paper on the clinkering of coal: Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 211-212; Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 824-828.

gas furnace. After heating the furnace, the blast is applied rapidly at first until the temperature is nearly that at which the cone begins to bend. Then the heat is regulated carefully and temperature readings with an optical pyrometer made every five minutes or oftener, depending upon the rate of heating; care must be taken to have the heating carried on slowly. As soon as the cone shows signs of bending, the temperature is noted and the operation continued until the cone has completely bent over and touched the plate, the temperature at which the cone touches the plate being called the fusing temperature.

Palmenberg prefers using long, thin cones, which in his experience are not subject to "separation of the more fusible constituents," an objection raised by Marks against the vertical-cone method. In regard to the effect of unburned carbon in the ash, Palmenberg states that this depends on the conditions of the tests and the nature of the ash; he found that as much as 10 per cent carbon had no effect, as seemingly it all burned off before the fusion took place.

#### E. B. RICKETTS, 1915.

Ricketts<sup>a</sup> describes the Seger-cone method as used in the laboratory of the New York Edison Co. as follows:

About 2 pounds of coal is coked in a crucible in a gas furnace for about an hour, after which the lump of coke is broken up and a stream of compressed air is fed in near the bottom of the crucible for from two to three hours until the coke is all reduced to ash. When burning the coke down, care should be taken to keep the temperature below 1,500° F. (820° C.), so as to prevent premature fusion. The ash is then tested, a small amount at a time, with oxygen to make sure that all the carbon is consumed. It is of vital importance that no carbon be left in the ash as a small trace may cause results several hundred degrees too high. The carbon-free ash is moistened with a little water and molded in a paper cone 2½ inches long and ½-inch base. The cone is dried for five or six hours and then fused in a muffle furnace without removing the paper in which it was molded. The cone is mounted horizontally so that it overhangs the point of support about 1½ inches. The point of fusion is taken when the cone reaches a 45° position and is read on a Wanner optical pyrometer.

The furnace consists of a gas melting furnace of 8 inches inside diameter. It is heated by horizontal blast burners which direct the flame around and over a covered Hessian crucible containing the ash cone. Observation of the interior of this crucible and of the cone is made through a suitably placed quartz tube which passes through the side of the melting furnace and the Hessian crucible.

Ricketts states further that with this method results of different tests of the same sample of coal corresponded within a few degrees and that the boiler tests with Babcock & Wilcox boilers fired with a Taylor stoker, showed a relation between efficiency of furnace and boiler and the fusion temperature of the ash. Thirteen coals were tested; the ash-fusion temperatures being between 2,225° F. (1,220°

<sup>a</sup> Ricketts, E. B., Discussion of paper on the clinkering of coal: Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 213-214; Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 830-834.

C.) and  $2,850^{\circ}$  F. ( $1,570^{\circ}$  C.). Those coals whose ash fused below  $2,375^{\circ}$  F. ( $1,300^{\circ}$  C.) gave a distinctly lower efficiency than those whose ash fused above  $2,450^{\circ}$  F. ( $1,345^{\circ}$  C.). The clinkering effect of coals whose ash-fusion temperatures were between the two temperatures mentioned was doubtful. The results of ash-fusion tests of coal from several hundred cargoes, from some 25 different sources, were said to confirm consistently the results of the earlier tests.

### COMPOSITION OF ASH AND DISTRIBUTION OF ASH-FORMING CONSTITUENTS IN COAL.

Ash is the incombustible residue left from the complete combustion of the carbon in coal. It is derived from the inorganic matter in the coal, and is composed largely of compounds of silica, alumina, iron, lime, together with smaller quantities of magnesia, titanium, alkali, sulphur, and phosphorus compounds. The silica, alumina, and titanite oxide are derived from sand, clay, shale, and slate, the iron oxide mainly from iron pyrite, and the lime and magnesia from their corresponding sulphates and carbonates.

As shown in the ash analyses given in Table 2 (p. 27), the chemical composition varies so widely that no typical composition can be given. Probably the analyses of most samples of coal ash will come between the following limits:

*Typical limits of ash analyses.*

Constituent.	Per cent.
SiO <sub>2</sub> -----	40 to 60
Al <sub>2</sub> O <sub>3</sub> -----	20 to 35
Fe <sub>2</sub> O <sub>3</sub> -----	5 to 25
CaO -----	1 to 15
MgO -----	0.5 to 4
Na <sub>2</sub> O+K <sub>2</sub> O -----	1 to 4

The ash-forming constituents consist of (1) "inherent" or "intrinsic" impurities that are present in an intimate mixture with the coal substance, and are derived either from the original vegetable material or from external sources by sedimentation, precipitation, or aeolic action during the process of accumulation of coal-forming vegetation; (2) impurities formed either during or after the laying down of the coal bed, which occur in the form of partings, veins, and nodules of clay, shale, slate, pyrite and calcite; and (3) impurities that become mechanically mixed with the coal in the process of mining, such as fragments of roof and floor.

### INTRINSIC ASH.

The ash-forming constituents comprising the intimately mixed impurities may be obtained by placing coarsely crushed coal in a solution of calcium or zinc chloride having a specific gravity of 1.35. The coal will float, and the heavier extraneous impurities will



sink. In some coals the percentage of intrinsic ash is so low that the ash-forming constituents must have come almost wholly from the coal-forming vegetation. A noteworthy example of coal exceptionally low in ash is that in the Sewell bed of West Virginia; several mine samples taken from this bed near Beckley, in Raleigh County, showed on analysis 1.5 to 2 per cent ash. Ordinarily the intrinsic ash is between 2 and 8 per cent, although in many coals it may reach a fairly high percentage, especially in bony coals, which yield 25 to 40 per cent ash.

In the minute joints or cleavage planes of certain coals are thin flakes of calcite, gypsum, silica, or clay, and some coals, as certain Arkansas coals, have veinlets of pyrite. These impurities are not intimately mixed with the coal substance, but yet can not be separated from the coal by any commercial methods of preparing the coal for use. Microscopic crystals of pyrite are also found distributed to such an extent in some coals that washing produces no appreciable lowering of the sulphur content.

The "intrinsic" ash may be either more or less fusible than the total ash of the coal as mined, depending on the composition of the two kinds of ash. In general, the ash from a coal having a high intrinsic ash content, such as is found in bony coal, is less fusible than the ash from a coal having low intrinsic ash content, as the high ash content is due to an intimate admixture of siliceous or argillaceous silt, which increases the softening temperature. On the other hand, a coal of normally low intrinsic ash content, containing well distributed microscopic crystals of pyrite, or joints filled with flakes of calcite, gypsum, or pyrite, is likely to form troublesome clinkers when burned. Such a coal contains well mixed and finely divided essential constituents of an easily fusible slag.

#### EXTRANEOUS ASH.

The percentage of ash derived from extraneous impurities varies considerably, depending on the number and size of the partings in the seam, the possibility of separating these from the coal, and the care with which the coal is mined. Impurities of this character may be removed to some extent by suitable methods of washing, picking, or screening. The possibility of improving the quality of coal by washing may be determined by the laboratory float-and-sink test already described; also, by determining the fusibility of the ash of the raw coal, as compared with that of the float coal, the effect of better preparation on the fusibility of the ash may be determined.

Better preparation may either increase or decrease the ash fusibility, depending on the fusibility of the intrinsic ash and the nature of the extraneous impurities. Such extraneous impurities as slate,

sandstone, or shale tend to raise the softening temperature; limestone and pyrite tend to lower the softening temperature, although limestone, if added in excess, will increase the softening temperature. Experience has shown that many of the best low-ash coals form very troublesome clinkers. A very fusible intrinsic ash would be expected to give excessive trouble in the fuel bed, as the various constituents are finely divided and intimately mixed in the coal, thus making a favorable condition for slag formation. It is doubtful whether large lumps of extraneous impurities have much influence on slagging in the furnace. Large pieces of slate are usually found unfused in the refuse.

## NATURE OF FUSION OF ASH.

### MELTING POINTS OF PRINCIPAL CONSTITUENTS OF ASH.

According to Day and Sosman,<sup>a</sup> "the melting point of a pure substance may be defined as the temperature at which the crystalline and liquid substance can remain side by side in equilibrium. Only the addition or withdrawal of a quantity of heat will cause the disappearance of one of the two forms in contact. Melting is therefore characterized by two concurrent changes, the appearance or disappearance of a particular crystal structure, and the appearance or disappearance of a quantity of heat. This definition applies to pure compounds. If the material is a mixture or a solid solution, it will have, not a melting point, but a melting interval, with (theoretically) definite temperature limits."

According to this definition, the principal constituents of coal ash, considered by themselves and in their crystalline form, have melting points well above the temperature at which fusion in the mixed ash is known to begin. Quartz ( $\text{SiO}_2$ ) at temperatures above  $1,600^\circ \text{C}$ . changes rapidly into cristobalite, which melts at about  $1,625^\circ \text{C}$ .<sup>b</sup>

At this temperature the rate of melting is very slow; and the fused silica has such a high viscosity that it does not flow or change shape distinctly until a temperature of  $1,750^\circ \text{C}$ . is reached.<sup>c</sup>

Pure alumina ( $\text{Al}_2\text{O}_3$ ) melts at  $2,050^\circ \text{C}$ .<sup>d</sup>

Kaolinite ( $\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$ ), the crystalline form of the essential constituent of clay, is unstable at high temperatures and appears to decompose into aluminum silicate ( $\text{Al}_2\text{O}_3, \text{SiO}_2$ ) and free silica.

<sup>a</sup> Day, A. L., and Sosman, R. B., The melting points of minerals in the light of recent investigations on the gas thermometer: *Am. Jour. Sci.*, vol. 31, 1911, p. 342.

<sup>b</sup> Fenner, C. N., The stability relations of the silica minerals: *Am. Jour. Sci.*, vol. 36, 1913, pp. 331-384.

<sup>c</sup> Kanolt, C. W., Melting points of fire bricks: U. S. Bur. Standards Tech. Paper 10, 1912, p. 14.

<sup>d</sup> Kanolt, C. W., Melting points of some refractory oxides: U. S. Bur. Standards Bull., vol. 10, 1913, p. 15.

Sillimanite ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ) melts at  $1,816^\circ \text{C}.$ <sup>a</sup> Kanolt<sup>b</sup> found the temperature of visible flowing of an English white kaolin to be  $1,740^\circ \text{C}.$  A sample of brownish-white German kaolin began flowing at  $1,735^\circ \text{C}.$  Lime ( $\text{CaO}$ ) melts at  $2,572^\circ \text{C}.,$ <sup>c</sup> and magnesia ( $\text{MgO}$ ) at  $2,800^\circ \text{C}.$ <sup>d</sup>

According to Sosman<sup>e</sup>—

Ferric oxide ( $\text{Fe}_2\text{O}_3$ ) begins to dissociate, as the temperature rises, into oxygen and a solid solution containing ferrous iron; this may be considered as a solid solution of  $\text{Fe}_3\text{O}_4$  in  $\text{Fe}_2\text{O}_3$ . At a given temperature the initial dissociation is high, but it drops rapidly as the percentage of  $\text{FeO}$  in the solid increases, passing through a range in which the pressure falls rather slowly with change of composition and finally falling rapidly to the dissociation pressure of  $\text{Fe}_3\text{O}_4$ , which is very low (less than 0.04 mm. of mercury at  $1,200^\circ \text{C}.$ ).

$\text{Fe}_3\text{O}_4$ , in turn, dissociates into oxygen and a mixture of oxides whose character has not yet been determined.

The properties of  $\text{FeO}$  are still practically unknown. The most of the recorded methods for preparing "ferrous oxide" yield only a mixture of metallic iron (or iron carbide) with an oxide whose composition falls between  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$ .

The melting point of magnetic ( $\text{Fe}_3\text{O}_4$ ) is  $1,580^\circ \text{C}.$ <sup>f</sup>

#### RELATION OF MELTING POINTS OF ASH CONSTITUENTS TO FUSION IN THE MIXTURE.

It is evident that coal ash, being a mixture of a number of substances both crystalline and amorphous, can have no single, definite melting point; neither is the gradual softening and fusion of the ash merely the successive melting of the various ash constituents, but it is a more complicated process in which reactions involving the formation of new and more fusible compounds take place. Furthermore, the melting temperature of these newly formed compounds is influenced by solution in one another to a greater or less degree, as in the familiar example of salt and ice. Pure water freezes at  $0^\circ \text{C}.$  If increasing quantities of salt are added to the water the freezing point is depressed more and more until a certain minimum freezing point is reached after which further addition of salt causes the freezing point to rise again. This minimum freezing point of a mixture is known as the eutectic point, and the composition of the mixture at this point is known as the eutectic composition.

<sup>a</sup> Shepard, E. S., and Rankin, G. A., The binary systems of alumina, silica, lime, and magnesia: *Am. Jour. Sci.*, vol. 28, 1909, pp. 293-333; *Ztschr. anorg. Chem.* Bd. 68, 1910, pp. 370-420.

<sup>b</sup> Kanolt, C. W., Melting points of fire bricks: *U. S. Bur. Standards Tech. Paper* 10, 1912, p. 14.

<sup>c</sup> Kanolt, C. W., Melting points of some refractory oxides: *U. S. Bur. Standards Bull.*, vol. 10, 1913, p. 19.

<sup>d</sup> Kanolt, C. W., Place quoted.

<sup>e</sup> Sosman, R. B., The common refractory oxides: *Jour. Ind. and Eng. Chem.*, vol. 8, 1916, p. 985.

<sup>f</sup> Sosman, R. B., The common refractory oxides: *Jour. Ind. and Eng. Chem.*, vol. 8, 1916, p. 985.



## FORMATION OF COMPOUNDS AND EUTECTICS AS ILLUSTRATED IN LIME-SILICA SYSTEM.

The compounds formed on heating and cooling various mixtures of two components, with their melting and transformation points, are enumerated in figure 1, which is a concentration-temperature diagram for the lime-silica system.<sup>a</sup>

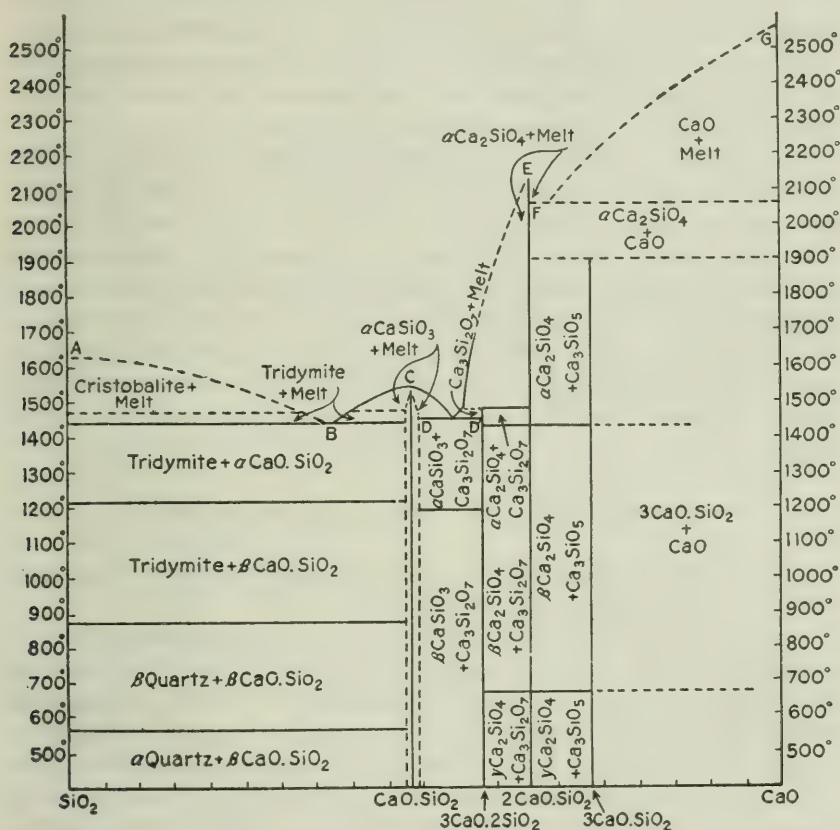


FIGURE 1.—Concentration-temperature diagram for the lime-silica system.

The melting point of pure silica in the form of cristobalite is given as 1,625° C. The melting point of pure calcium oxide (CaO) is given as 2,570° C. As increasing percentages of CaO are added to the SiO<sub>2</sub> the melting point is gradually depressed until at the point B a minimum or eutectic point is reached. The eutectic composition is 37 per cent CaO and 63 per cent SiO<sub>2</sub>, and the melting point of the eutectic is 1,436° C. A further addition of lime increases the

<sup>a</sup> Rankin, G. A., and Wright, F. E., The ternary system CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>: Am. Jour. Sci., vol. 39, 1915, p. 5.

melting point until at C a maximum is reached at  $1,540^{\circ}\text{C.}$ , which is the melting point of the compound pseudowollastonite ( $\alpha\text{CaSiO}_3$ ), containing 48.2 per cent CaO and 51.8 per cent  $\text{SiO}_2$ . Any mixture of silica and lime between the points A and B and between the points B and C will show evidence of fusion when the temperature reaches  $1,436^{\circ}\text{C.}$ , the melting point of the eutectic; as at this temperature that part of the mixture which is present in eutectic proportion (37CaO to 63 $\text{SiO}_2$ ) will melt, leaving an excess of one or the other component unmelted. The nearer the mixture as a whole approaches the eutectic composition, the greater the proportion that melts at the eutectic temperature.

The point E,  $2,130^{\circ}\text{C.}$ , represents the melting point of the alpha form of calcium orthosilicate ( $\alpha\text{Ca}_2\text{SiO}_4$ ). Another eutectic occurs between the points E and C, and a third between E and G.

Figure 1 shows that in mixtures of CaO and  $\text{SiO}_2$  there are possible two compounds and three binary eutectics having definite melting points. All other ratios of CaO and  $\text{SiO}_2$  than these five have a melting interval rather than a melting point. The interval is between the melting point of the eutectic and the temperature represented by the upper curve, A B C, at which all the material has become liquid.

#### DETERMINATION OF THE MELTING INTERVAL.

It is possible to determine this melting interval by the "quenching method" of the geophysical laboratory.<sup>a</sup>

By this method a small charge of the mixture is held at a definite temperature until equilibrium is insured, when the melted mixture is dropped suddenly into a basin of mercury, in which it is instantly cooled before any crystallization can occur. The degree of melting for the given temperature is shown by the percentage of glass found when the melted mixture is examined under the microscope. By repeating the test several times at different temperatures the melting interval may be determined.

#### RELATION OF MELTING INTERVAL TO CLINKER FORMATION.

The quenching method, although undoubtedly the only scientific method of determining the degree of melting at any given temperature, does not give any information regarding the viscosity of the fusion, and therefore would not in itself serve as a practical technical test of probable clinkering characteristics. As regards clinker formation, information is desired as to the temperature at which the

<sup>a</sup> Day, A. L., and Sosman, R. B., The melting points of minerals in the light of recent investigations on the gas thermometer: *Am. Jour. Sci.*, vol. 31, 1911, p. 343.

ash may form a slag of sufficient fluidity to flow or agglomerate in the fuel bed; this temperature is usually below the temperature of complete melting as shown by the quenching method, owing to the formation of low-melting eutectics, as already described.

The difference between the flowing or softening temperature and the temperature of complete melting varies greatly in different ashes, depending on the relative proportion of initially melting eutectic and the viscosity of this initial slag. If this slag is very fluid it may flow readily to form clinkers, and yet contain a considerable proportion of solid constituents in suspension. On the other hand, if the ash were composed almost wholly of alumina and silica, it could be completely melted and yet not flow readily, owing to its high viscosity. Hence, any laboratory method of determining the fusibility of ash, together with the degree of clinker formation, should indicate the viscosity as well as the melting temperatures. A theoretically correct method would be one in which the viscosity-temperature curve of the melt for blast-furnace slags is determined, as has been done by one of the authors.<sup>a</sup> This method is not available, as when it is used the iron oxides are reduced by the graphite parts of the apparatus. Probably the simplest method of roughly determining the temperature at which the melting ash forms a slag of standard viscosity is the usual softening-temperature test, which is employed by the metallurgist in determining the "formation temperature" of slags.<sup>b</sup>

#### DETERMINATION OF SOFTENING TEMPERATURE.

Determination of the softening temperature of an ash is usually made by molding the ash in the form of a small triangular pyramid similar to a Seger cone, and noting the temperature of deformation when the cone is heated at a definite rate. The temperature at which the cone has bent over until the apex touches the base, or at which it collapses to a lump, is taken as the softening point.

Day and Shepard<sup>c</sup> have shown that a cone made of silicate mixtures that are capable of forming eutectics begins to weaken as soon as the eutectic begins to melt; its further progress is then governed entirely by the relative quantity of eutectic present and its viscosity after melting. If the constituents of the ash are such as to form a relatively large proportion of thinly fluid eutectic, the deformation point of the cone will lie close to the melting point of the eutectic; on the

<sup>a</sup> Feild, A. L., A method for measuring the viscosity of blast-furnace slags at high temperatures: Tech. Paper 157, Bureau of Mines, 1916, p. 21.

<sup>b</sup> Fulton, C. H., Principles of metallurgy, 1st ed., 1910, p. 274.

<sup>c</sup> Day, A. L., and Shepard, E. S., The lime-silica series of minerals: *Am. Jour. Sci.*, vol. 22, 1906, p. 267. Also, for a full discussion of the theory of Seger cones, see Sosman, R. B., The physical chemistry of Seger cones: *Trans. Am. Cer. Soc.*, vol. 15, 1913, pp. 482-498.



other hand, if there is a large excess of some refractory component, as silica or aluminum silicate, or if the eutectic is viscous, the excess component will form a rigid skeleton, which is not pulled down by the eutectic, the deformation point approaching more nearly the melting point of the rigid component.

#### FACTORS INFLUENCING SOFTENING TEMPERATURE.

The whole phenomenon of softening and fusion of ash is a result of chemical reaction, melting, and solution, in which the time factor and the fineness of division of the constituents are of the greatest importance. Some reactions between ash constituents, and between certain oxides, with the atmosphere in which the ash is heated take place before any melting begins. Other reactions of various velocities make their appearance after incipient fusion. Also, certain constituents have a slow rate of melting, as, for example, silica and feldspar. These substances can be heated above their melting points and yet remain in a crystalline form for some time. It is obvious, then, that the softening temperature of an ash cone must be affected by (1) the size, shape, and inclination of the cone, (2) the fineness of the ash, (3) the rate of heating, and (4) the nature of the atmosphere in which the cone is heated.

#### INFLUENCE OF IRON OXIDES.

Owing to the invariable presence of iron oxide in coal ash, the nature of the surrounding gases—whether oxidizing or reducing—determines, in part, the rôle which the iron shall play in the slagging reactions. In the ordinary method of preparing a coal ash by burning off the carbon in air at a red heat the iron content is practically all converted to ferric oxide ( $\text{Fe}_2\text{O}_3$ ). As this oxide is heated in air it begins to dissociate at about  $1,100^\circ \text{C.}$ <sup>a</sup> forming a solid solution containing ferrous oxide ( $\text{FeO}$ ). The degree of dissociation increases with the temperature, so that ultimately all the ferric oxide is converted to magnetite ( $\text{Fe}_3\text{O}_4$ ) at approximately  $1,350^\circ \text{C.}$ <sup>b</sup> Therefore, in determining the softening temperature of an ash in air, with absolutely no reducing gases present, we are dealing with the formation of slags in which the iron component enters the reaction as ferric oxide or as a solid solution varying in composition from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . Such slags are more refractory and more viscous than those formed by heating mixtures

<sup>a</sup> Sosman, R. B., and Hostetter, J. C., The oxides of iron. Solid solution in the system  $\text{Fe}_2\text{O}_3\text{--Fe}_3\text{O}_4$ : Jour. Am. Chem. Soc., vol. 38, 1916, pp. 807–833; Hostetter, J. C., and Sosman, R. B., The dissociation of ferric oxide in air: Jour. Am. Chem. Soc., vol. 38, 1916, pp. 1188–1198.

<sup>b</sup> Walden, P. T., On the dissociation pressure of ferric oxide: Jour. Am. Chem. Soc., vol. 30, 1908, p. 1350.

under conditions favoring the formation of ferrous iron. Peters<sup>a</sup> states that—

Ferric oxide forms compounds with silica which require a high temperature for their fusion, and is consequently an unwelcome base for slags; although this substance is an almost invariable constituent of oxidized ores, it seldom makes any trouble in the blast furnace, for the reason that it is easily reduced by the fuel gases to ferrous oxide (FeO).

In the more neutral atmospheres of the reverberating smelter, however, it is likely to cause delay by combining with silica, making it more difficult to melt the slag.

On the other hand, if the ash cone is heated in a reducing atmosphere of hydrogen and water vapor<sup>b</sup> or carbon monoxide and carbon dioxide, the ferric oxide is reduced largely to ferrous oxide, which is a much stronger fluxing agent than the higher oxides of iron. Steffe<sup>c</sup> found the following formation temperatures for various ferrous silicates and ferro-calcic silicates:

*Formation temperatures of ferrous and ferro-calcic silicates, after Steffe.*

Compound.	Formation temperature, ° C.
4FeO, SiO <sub>2</sub> -----	1, 158-1, 174
2FeO, SiO <sub>2</sub> -----	1, 162-1, 183
4FeO, 3SiO <sub>2</sub> -----	1, 162-1, 181
FeO, SiO <sub>2</sub> -----	1, 158-1, 171
2FeO, 3SiO <sub>2</sub> -----	1, 321-1, 334
2(FeO, CaO)SiO <sub>2</sub> -----	1, 122-1, 137

As shown by Greiner,<sup>d</sup> the viscosity of ferrous silicate slags is lower than that of slags in which the iron component enters the reaction in the ferric form. Hence, the conclusion seems logical that in general lower softening temperatures may be expected if, before fusion begins, the atmosphere surrounding the cone is able to reduce most of the iron to the ferrous state, but not to metallic iron, for, if the iron is reduced to the metallic state, one of the most active fluxing constituents is removed from the system. Most ashes have an excess of high-melting constituents like silica and alumina, so that any considerable reduction of iron oxide to metallic iron tends to increase the refractory effect of the silica and alumina. Hence, lower softening temperatures may be expected in tests made in gas furnaces, in which some reducing gases come in contact with the ash, whereas higher results should be found both in furnaces in which air only surrounds the cone, and in carbon or graphite electric furnaces in which strongly reducing atmospheres reduce the iron oxides to metallic iron.

<sup>a</sup> Peters, E. D., Principles of copper smelting: New York, 1907, pp. 399-400.

<sup>b</sup> Hilpert, S., and Beyer, J., Ber. deut. chem. Gesel., Jahrg. 44, 1911, pp. 1608-1619.

<sup>c</sup> Steffe, Herman, Ueber die Bildungs temperaturen einiger Eisenoxydul-Kalkschlacken und einiger kalkfreien Eisenoxydul-Schlochen, deren Kenntniss für das Verschmelzen der Bleierze Bedeutung hat: Dissertation, Berlin, 1908.

<sup>d</sup> Greiner, E., Ueber die abhängigkeit der Viscosität in Silikat Schmelzen von ihrer Zusammensetzung: Inaugural dissertation, Jena, 1907, p. 55.

## EXPERIMENTS WITH SEGER CONES.

## DESCRIPTION OF FURNACES.

In studying the effect of various factors on the softening temperature of ash, the authors made tests with a selected series of coal ashes

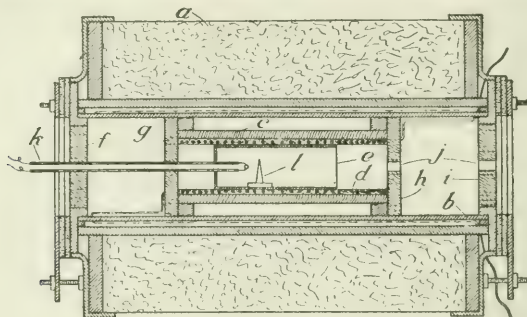


FIGURE 2.—Section through platinum-wire resistance furnace. *a*, Heraeus tube furnace, type B; *b*, porcelain tube, 2½ inches in inside diameter and 12 inches long, wound with a platinum-foil heating element; *c*, alumina tube, 1½ inches in inside diameter and 6 inches long, with ⅜-inch wall; *d*, 17 feet of platinum wire 3/100 of an inch in diameter, wound on the inside of tube *c*, six turns to the inch in the middle and closer at the ends to compensate partly for the radiation at the ends; *e*, alumina extraction thimble No. 5811, 30 mm. in diameter and 80 mm. long; *f*, *g*, and *h*, *i*, alumina disks; *j*, observation hole; *k*, thermo element made of platinum and platinum-rhodium; *l*, ash cone.

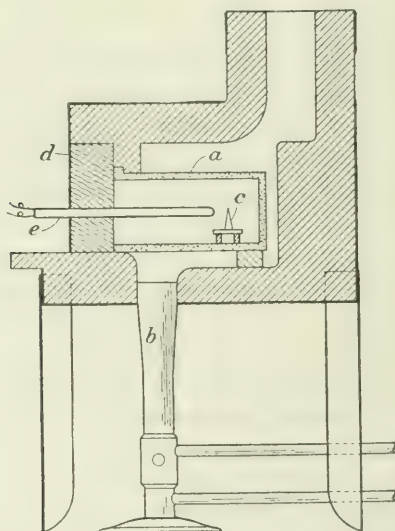


FIGURE 3.—Meker muffle furnace No. 29. *a*, Magnesite muffle; *b*, Meker blast burner; *c*, ash cone; *d*, removable fire-clay door with horizontal slot for thermocouple tube *e*.

in different types of furnaces such as are in more or less common use for such tests. Each of these furnaces has its own particular atmosphere—oxidizing, reducing, or neutral—which is the principal cause



of the large variations that were found on comparing the softening temperatures of the same sample in the different furnaces.

In the comparative tests six furnaces were used, as follows:

1. Platinum-wire resistance furnace (fig. 2), having an oxidizing atmosphere of air, with absolutely no reducing gases present.

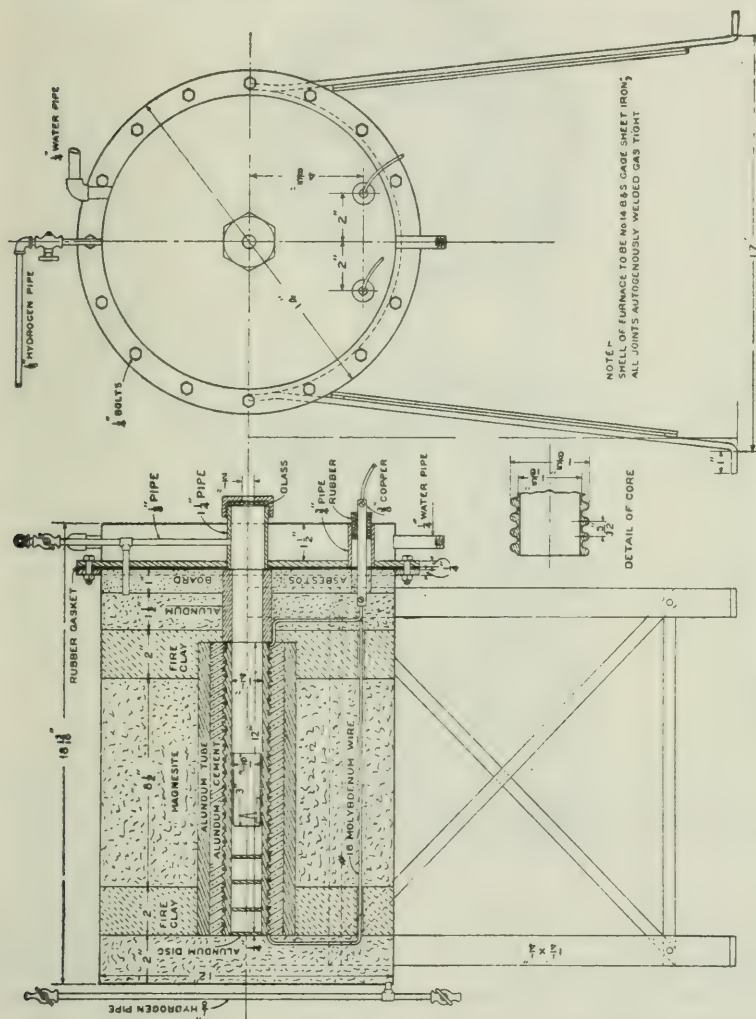


FIGURE 4.—Molybdenum furnace.

2. Meker muffle furnace No. 29 (fig. 3), having an atmosphere of air and combustion gases.

3. Muffle furnace No. 2, having an atmosphere of air and combustion gases.

4. Molybdenum-wire resistance furnace (fig. 4), having a reducing atmosphere of hydrogen.

5. Granular-carbon resistance furnace (fig. 5), having a reducing atmosphere of carbon monoxide.

6. Northrup graphite resistance furnace (fig. 6), having a reducing atmosphere of carbon monoxide.

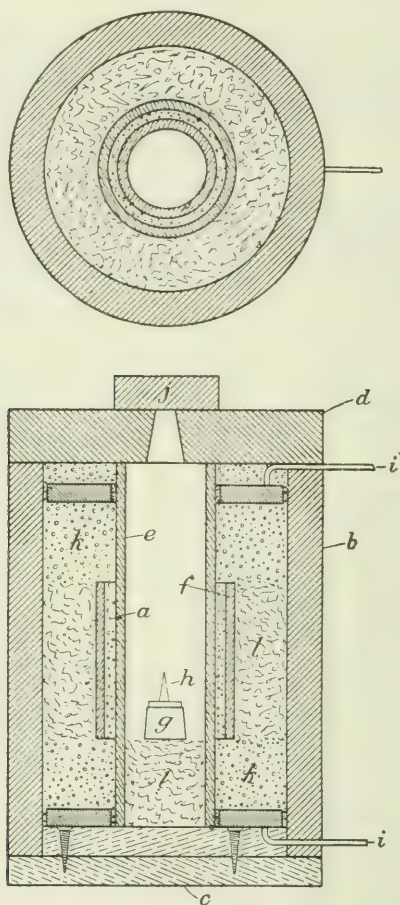


FIGURE 5.—Granular-carbon resistance furnace. *a*, Granular-carbon resister, consisting of electrode carbon crushed to pass a 6-mesh and remain on a 12-mesh screen; *b*, fire-clay cylinder, 8 inches in external diameter, 10 inches high, 1-inch wall; *c*, transit base,  $\frac{3}{4}$  inch thick; *d*, fire-clay cover plate, 2 inches thick; *e*, alundum tube, 2-inch bore, 9 inches long,  $\frac{1}{4}$ -inch wall; *f*, alundum tube, 3-inch bore, 4 inches long,  $\frac{1}{8}$ -inch wall; *g*, inverted alundum crucible; *h*, ash cone; *i*, *i*, wrought-iron electrodes; *j*, fire-clay plate covering peephole; *k*, granular carbon; *l*, magnesia insulating material.

Before studying the results obtained in each furnace, as presented in the following pages, the reader is invited to notice the general method of operating the furnaces as outlined in the titles of the figures showing them.

## DESCRIPTION AND ANALYSES OF COAL SAMPLES USED IN TESTS.

The description and origin of the coal samples are given in Table 1 following, and the analyses of the ash and partial analyses of the coal in Table 2 following. As may be seen from an inspection of these tables, the series of fuels tested include anthracite, bituminous,

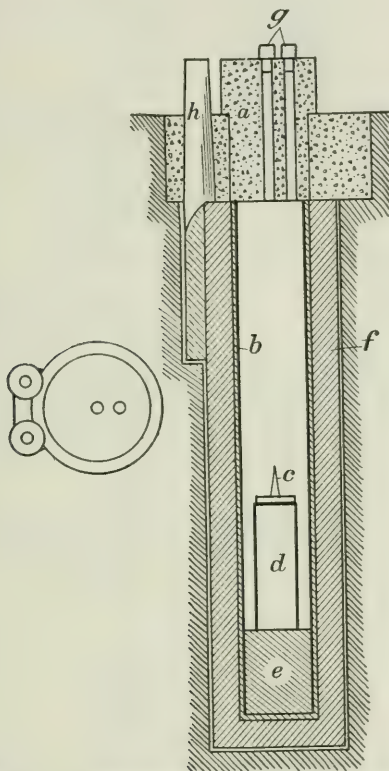


FIGURE 6.—Arrangement for softening temperature test in Northrup furnace. *a*, Refractory plug; *b*, graphite tube for protecting heater from oxidation,  $1\frac{3}{8}$  inches in internal diameter,  $12\frac{3}{4}$  inches long; *c*, ash cone; *d*, inverted alundum extraction capsule, 3 inches high; *e*, solid graphite cylinder, 2 inches high; *f*, graphite heater unit; *g*, observation holes,  $\frac{1}{4}$  inch in diameter; *h*, terminal of graphite heater unit.

semibituminous, and subbituminous coal, lignite, and peat; the composition of the ash covers a fairly wide range, the silica content varying from 12.3 to 76 per cent; alumina from 8.6 to 34.7; ferric oxide from 3.8 to 69.7; lime from 0.6 to 18.6; and magnesia from 0.2 to 10 per cent.



TABLE 1.—Character and source of coal samples.

Sample No.	Lab. No.	Kind of coal.	Coal bed.	Location of mine.		
				Nearest town.	County.	State.
1	15840	Bituminous	Coal Creek	Fraterville	Anderson	Tenn.
2	15841	do.	American	Parrish	Walker	Ala.
3	15842	do.	Sterling	Manring	Claiborne	Tenn.
4	15843	do.	Jellico	Jellico	Campbell	Do.
5	15844	do.	Mingo	Fork Ridge	Claiborne	Do.
6	15845	do.	Coal Creek	Oliver	Morgan	Do.
7	15846	do.	Mary Lee	Red Star	Walker	Ala.
8	15847	do.	Nickel Plate	Jefferson	Jefferson	Do.
9	15848	do.	Thompson	Marvel	Bibb	Do.
10	16018	do.	Red Stone	Lemely Junction	Barbour	W. Va.
11	16019	do.	Pittsburgh	Morgantown	Monongalia	Do.
12	16243	do.	No. 5	Booneville	Warlick	Ind.
13	16583	Semibituminous	Pocahontas No. 3	Simmons	Mercer	W. Va.
14	16584	do.	do.	Bramwell	do.	Do.
15	16585	do.	do.	Elk Ridge	McDowell	Do.
16	16586	do.	do.	Big Four	do.	Do.
17	16587	do.	do.	Jenkin Jones	do.	Do.
18	16589	do.	do.	Boisevain	Tazewell	Va.
19	17081	Anthracite (buckwheat).				Pa.
20	17189	do.		Shenandoah	Schuylkill	Do.
21	17534	do.			Luzerne	Do.
22	17590	do.		Shamokin	Northumberland	Do.
23	18248	do.				Do.
24	14762	do.				Do.
25	17563	Semibituminous	Lower Kittanning	Lonaconing	Alleghany	Md.
26	a 7244	do. b	Pocahontas No. 3	Pocahontas	Tazewell	Va.
27	a 7305	do. b	do.	do.	do.	Do.
28	7308	do. b	do.	do.	do.	Do.
29	c 7309	do. b	do.	do.	do.	Do.
30	18193	do.	do.	do.	do.	Do.
31	18198	do.	do.	do.	do.	Do.
32	18203	do.	do.	do.	do.	Do.
33	18349	do.	do.	do.	do.	Do.
34	18350	do.	do.	do.	do.	Do.
35	18208	do.	Lower Kittanning	Ebensburg	Cambria	Pa.
36	18296	do.		Bering River Field		Alaska.
37	18297	do.		do.		Do.
38	18298	do.		do.		Do.
39	18302	do.		do.		Do.
40	18308	do.		do.		Do.
41	18310	do.		do.		Do.
42	18312	do.		do.		Do.
43	18300	do.		do.		Do.
44	18303	do.		do.		Do.
45	18306	do.		do.		Do.
46	18348	do.		do.		Do.
47	18347	do.		do.		Do.
48	18350	do.		do.		Do.
49	12690	Bituminous	Pittsburgh	Greensburg	Westmoreland	Pa.
50	c 12691	do.	do.	do.	do.	Do.
51	a 7228	do.	do.	Marianna	Washington	Do.
52	7230	do.	do.	do.	do.	Do.
53	a 7141	do.	do.	do.	do.	Do.
54	c 7458	do.	do.	Carnegie	Alleghany	Do.
55	13316	Subbituminous		Batan	Philippine Islands	
56	c 7548	Lignite		Rockdale	Milan	Tex.
57	a 7381	do.		do.	do.	Do.
58	a 7490	do.		Lytie	Medina	Do.
59	a 7494	do.		do.	do.	Do.
60	c 7522	do.		Calvert	Robertson	Do.
61	7534	do.		do.	do.	Do.
62	a 7536	do.		do.	do.	Do.
63	a 7159	Peat briquets		Elizabeth City	Pasquotauk	N. C.
64	17559	Bituminous	Widow Kennedy	do.	Dickinson	Va.
65	17560	do.	do.	do.	do.	Do.
66	18121	do.	do.	Dante	Russell	Do.
67	19514	Semibituminous	Lower Kittanning or B.	Colver	Cambria	Pa.
68	19817			Stoke-on-Trent	Birchenwood Collieries	England.
69	19818	Semibituminous	Pocahontas			China.
70	19841					Do.
71	19842					Do.
72	20021	Bituminous			Matanuska field	Alaska.
73	20022	do.			do.	Do.
74	20023	do.			do.	Do.
75	20153	do.	Anderson	West Fork Station	Coos	Oreg.

a Clinker from gas producer.

b Bone coal.

c Clinker from boiler furnace.

TABLE 1.—*Character and source of coal samples—Continued.*

Sample No.	Lab. No.	Kind of coal.	Coal bed.	Location of mine.		
				Nearest town.	County.	State.
76	20191	Semibituminous.	Pocahontas.			W. Va.
77	20204	do.	do.			Do.
78	20217	do.	do.			Do.
79	20851	do.	Sewell.	Dunlap and Prudence.	Fayette.	Do.
80	20852	do.	do.	do.	do.	Do.
81	20853	do.	do.	do.	do.	Do.
82	20913	Bituminous.	Jellico.		Campbell.	Tenn.
83	20914	do.	Coal Creek.		Anderson.	Do.
84	21328	Semibituminous.		Huntington.	Sebastian.	Ark.
85	21895	Bituminous.	Upper and Lower Banner.	Dante.	Russell.	Va.
86	22665	Semibituminous.	Lower Kittanning or B.	Nanty Glo.	Cambria.	Pa.
87	22855	Bituminous.	Lower Weir-Pittsburg.	Frontenac.	Crawford.	Kans.
88	22988	do.	Saginaw.	Akron.	Tuscola.	Mich.
89	22991	do.	No. 6.	Duquoin.	Perry.	Ill.
90	23014	do.	No. 2.		Saginaw.	Mich.
91	2 S. A.	Semianthracite.	Spadra.		Johnson.	Ark.
92	3 Poca.	Semibituminous.	Pocahontas No. 3.		McDowell.	W. Va.
93	4 S. B.	do.	Sewell.		Fayette.	Do.
94	6 Wash.	Bituminous.			Pierce.	Wash.
95	9 Ill.	do.	Herrin or No. 6.		Macapin.	Ill.
96	10 Wyo.	Subbituminous.	Carney.		Sheridan.	Wyo.
97	11 Lig.	Lignite.			Williams.	N. Dak.
98	13629	Bituminous.	Freeport.	New Kensington.	Westmoreland.	Pa.
99	23331	do.	Pittsburgh.		Washington.	Do.
100	23507	do.	Freeport.	New Kensington.	Westmoreland.	Do.
101	19159	Semibituminous.				W. Va.
102	10155	do.				Do.
103	19161	do.				Do.
104	22934	Bituminous.	Lower Kittanning.	Vintondale.	Cambria.	Pa.
105	23136	do.		Castle Gate.	Carbon.	Utah.
106	23137	do.		Sunnyside.	do.	Do.
107	23138	do.		Clear Creek.	do.	Do.
108	23581	do.	Pittsburgh.	Blaine.	Allegheny.	Pa.
109	25366	do.		Diamond.	Washington.	Do.
110	23370	do.		Hale and Lady-smith.	Clearfield.	Do.
				Norfolk No. 3.	McDowell.	W. Va.

a Clinker from gas producer.

TABLE 2. *Analyses of ash and coal.*

Lab. No.	Sample No.	Analyses of ash.										Analyses of dry coal.		
		SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .a	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SO <sub>3</sub> .	Sulphur.	Ash.	Fe <sub>2</sub> O <sub>3</sub> .	
15840	1	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>		
15841	2	35.7	23.5	32.9	1.2	3.2	1.1	0.3	1.1	0.5	3.1	10.8	3.6	
15842	3	47.3	34.6	9.8	1.8	1.3	.4	2.1	2.5	.1	1.7	17.4	1.7	
15843	4	55.8	33.5	5.0	.9	1.5	.7	.5	2.2	.1	.8	15.6	.8	
15844	5	43.3	31.4	13.6	1.2	4.2	1.4	.6	2.9	1.4	1.5	8.6	1.2	
15845	6	42.2	30.6	19.0	1.2	1.3	1.0	1.3	2.9	.2	1.4	7.5	1.4	
15846	7	12.3	12.2	69.7	.4	3.9	.7	.3	.6	.2	5.8	8.2	5.7	
15847	8	54.1	34.7	4.5	1.5	1.2	.9	.6	2.5	.2	.7	17.7	.8	
15848	9	46.8	28.7	18.0	1.4	.6	.9	1.6	2.4	.3	2.3	12.7	2.3	
16018	10	54.8	27.0	7.0	1.3	4.3	1.7	.3	3.1	1.4	.6	17.5	1.2	
16019	11	38.4	24.2	22.4	1.1	7.7	.9	.3	1.9	3.8	2.1	7.9	1.8	
16243	12	50.4	24.0	20.4	1.4	1.7	.2	1.0	1.0	.3	2.7	10.9	2.2	
16583	13	37.1	17.6	35.9	.7	3.2	.9	.4	1.8	2.3	5.8	11.5	4.1	
16584	14	54.8	27.0	7.8	1.6	1.6	1.5	2.2	1.9	.5	.7	8.0	.6	
16585	15	54.8	29.2	6.9	1.8	1.4	.6	1.9	2.1	1.0	.7	7.5	.5	
16586	16	54.1	24.8	9.4	2.3	4.0	1.4	1.0	.8	2.8	.6	7.1	.7	
16587	17	37.2	25.5	11.8	1.5	12.6	1.9	1.4	.4	5.6	.6	5.9	.7	
16588	18	51.1	25.2	10.1	1.8	5.1	1.6	.8	.9	3.1	.6	6.8	.7	
16589	19	51.8	25.0	9.0	2.0	4.0	1.5	1.3	.8	4.3	.7	5.6	.5	
17081	20	56.1	31.4	5.0	1.9	1.0	1.0	.7	3.1	.5	.7	21.5	2.1	
7244	26	68.9	21.4	4.5	2.6	2.0	.7	.6	.5	.....	.6	17.2	.8	

TABLE 2.—Analyses of ash and coal—Continued.

Lab. No.	Sample No.	Analyses of ash.										Analyses of dry coal.			
		SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> <sup>a</sup>	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SO <sub>3</sub> .	Sulphur.	Ash.	Fe <sub>2</sub> O <sub>3</sub> .		
		<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>		
7305	27	69.4	21.5	4.8	2.0	1.6	.8	.5	1.4	.....	.7	14.8	.7		
7308	28	64.7	23.2	4.7	2.6	1.2	.8	.3	1.5	1.5	.7	14.8	.7		
7309	29	69.6	19.7	5.2	2.2	2.0	.4	.4	.5	.....	.7	14.1	.7		
12690	49	54.7	32.9	8.9	.....	1.6	.9	.6	.2	.....	.9	11.1	1.0		
7228	51	54.5	27.0	12.1	1.8	1.5	.4	.5	1.9	.....	1.7	11.4	1.4		
7230	52	53.2	26.0	15.8	1.4	1.0	.7	.3	1.6	.....	1.7	11.4	1.8		
7141	53	54.6	25.7	12.4	1.4	4.3	.6	.6	1.3	.....	1.4	12.5	1.6		
7458	54	56.8	28.2	11.3	1.2	1.0	.8	.6	1.6	.....	1.8	12.3	1.4		
13316	55	15.2	8.6	13.3	.....	18.1	10.0	5.3	1.8	26.9	.....	8.2	1.1		
7548	56	47.9	23.7	5.5	2.0	18.6	3.3	.4	.2	.....	1.5	16.6	.9		
7381	57	46.2	24.3	6.2	1.8	18.5	3.0	.6	.5	.....	1.5	15.5	1.0		
7490	58	43.2	16.9	7.1	1.6	12.2	1.7	.2	.3	16.0	2.2	19.1	1.4		
7494	59	52.5	21.5	8.8	1.6	14.4	2.4	.5	.2	.....	2.2	19.1	1.7		
7522	60	47.5	29.1	5.3	2.0	14.0	2.2	.4	.3	.....	1.4	18.6	1.0		
7534	61	39.3	24.8	3.8	1.9	14.9	1.7	.2	.4	12.5	1.4	16.6	.6		
7536	62	46.5	28.4	5.2	2.0	16.1	2.3	.7	.2	.....	1.4	16.6	.9		
7159	63	76.0	11.7	4.5	1.0	2.8	3.1	1.0	.9	.....	1.4	32.3	1.5		
19842	71	54.1	25.8	9.0	1.0	1.9	1.2	1.6	3.8	1.4	.6	12.4	1.1		
20021	72	49.9	29.1	10.0	1.1	3.7	1.4	.9	.7	2.5	.5	22.7	2.3		
20204	b 77	59.7	26.4	7.0	.....	2.6	1.3	.....	(c)	.....	.6	5.7	.4		
20217	b 78	56.3	25.9	9.5	.....	3.1	1.5	.....	(c)	.....	.6	6.2	.6		
20851	79	54.3	24.6	12.4	.....	1.4	.4	2.8	1.9	1.0	.9	7.4	.9		
20913	82	48.0	28.0	11.7	1.9	3.6	1.1	1.4	1.9	2.9	1.5	8.6	1.0		
20914	83	37.9	27.3	18.4	3.0	5.6	1.4	1.9	1.1	3.8	3.1	10.8	2.0		
21328	b 84	37.4	23.3	28.8	.....	3.8	3.0	.....	(b)	.....	2.3	9.5	2.7		
a 21895	b 85	38.8	25.5	7.9	1.3	12.1	2.4	2.5	1.7	8.3	.6	8.6	.7		
22665	b 86	31.0	22.7	41.9	.....	2.1	.9	.....	(b)	.....	3.1	8.2	3.4		
22855	87	34.2	14.6	31.5	.7	7.6	.9	1.1	1.5	6.5	5.0	19.0	6.0		
22991	89	32.0	25.9	13.4	1.1	2.5	.6	.8	1.6	1.8	1.8	11.2	.5		
13629	98	38.2	23.4	23.5	.....	5.6	1.1	5.3	1.4	2.9	2.9	12.5	2.9		
23507	100	42.7	25.6	18.9	1.2	5.2	.4	.7	1.3	4.2	2.4	11.9	2.2		
17559	64	50.5	29.2	9.3	2.1	1.8	2.1	.7	3.5	5.1	.7	11.2	1.0		
17560	65	47.8	27.0	13.6	2.1	2.4	1.7	.4	3.1	1.3	.7	8.4	1.2		
18121	66	31.9	23.2	19.6	1.8	9.8	1.1	.7	2.6	8.8	1.8	7.6	1.5		
19514	67	43.8	29.0	18.4	2.6	2.6	.2	.5	1.1	1.9	1.4	7.0	1.3		
19817	68	48.9	24.6	10.5	2.3	4.2	2.1	1.1	2.7	3.0	.9	14.2	1.5		
19818	69	49.8	25.5	9.6	1.7	3.8	2.5	1.3	3.3	2.6	.9	16.7	1.6		
19841	70	.....	.....	.....	.....	.....	.....	.....	.....	.....	.5	5.4	.....		
20022	73	51.3	25.9	8.3	2.3	5.1	3.0	1.1	1.1	2.4	.4	22.2	1.8		
20023	74	49.1	28.7	7.9	1.4	5.9	1.8	.6	.8	3.3	.4	13.3	1.1		
20153	75	55.9	24.9	6.5	3.5	3.5	.5	1.8	1.0	2.1	.9	21.7	1.4		
20191	76	54.2	22.5	8.4	3.9	4.0	1.0	1.7	1.1	3.5	.7	5.9	.5		
20852	80	46.2	27.9	18.4	2.0	2.0	.6	1.2	1.3	1.0	1.2	6.3	1.2		
20853	81	47.4	27.3	15.2	2.1	1.7	1.3	1.2	2.7	.8	1.0	7.2	1.1		
20913	82	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.0	5.5	.....		
20914	83	.....	.....	.....	.....	.....	.....	.....	.....	.....	1.6	7.0	.....		
21895	85	.....	.....	.....	.....	.....	.....	.....	.....	.....	.6	8.6	.....		
22988	88	17.8	15.6	59.8	.6	1.9	.5	1.1	.7	1.9	4.7	7.8	4.7		
23014	90	40.2	26.6	14.9	1.2	7.2	.7	.8	2.4	5.8	2.4	15.2	2.3		
2	91	11.0	27.5	34.6	1.4	10.7	3.1	.6	1.3	9.7	1.7	9.6	3.3		
3	92	59.3	21.9	5.9	6.2	1.9	.6	1.8	1.4	1.1	.6	7.4	.4		
4	93	40.8	25.8	24.5	3.1	2.6	.7	.8	.7	.8	.8	3.5	.9		
6	94	20.8	31.6	23.9	2.8	9.0	1.1	1.4	.8	8.6	.8	8.6	2.1		
9	95	58.6	21.7	7.5	3.3	2.7	.7	2.0	2.2	1.6	4.5	11.5	.9		
10	96	23.0	24.3	4.4	.7	20.6	3.0	3.8	.5	19.2	.5	5.2	.2		
11	97	7.7	12.1	6.9	.3	22.9	4.2	18.2	.6	26.8	.8	8.8	.6		
23331	99	46.3	22.7	10.8	1.3	8.7	.4	.7	1.1	7.5	1.5	12.3	1.3		
22934	104	30.3	24.6	37.9	1.3	3.0	.2	.5	.6	2.0	2.7	7.4	2.7		
23136	105	48.4	16.5	5.6	.....	14.5	2.6	2.1	.7	8.8	.4	5.4	.3		
23137	106	55.1	34.0	4.4	.....	4.1	.1	.7	.2	1.3	.7	5.3	.2		
23138	107	60.0	17.6	6.2	.....	7.0	.7	1.5	.4	6.4	.6	4.1	.3		
23581	108	48.0	24.7	11.6	1.8	5.8	.5	1.1	1.0	5.0	1.5	10.2	.....		
25366	109	42.5	31.8	19.6	1.8	2.1	.2	.8	.6	.9	1.5	8.8	.....		
25370	110	63.8	22.6	5.7	3.7	1.3	.7	.....	.7	.7	.5	10.0	.....		

<sup>a</sup> P<sub>2</sub>O<sub>5</sub> included with Al<sub>2</sub>O<sub>3</sub>. TiO<sub>2</sub> not determined separately but included with Al<sub>2</sub>O<sub>3</sub> in all cases where no result for TiO<sub>2</sub> is given.

<sup>b</sup> Analysis is not that of coal ashed in laboratory but of ashes taken from steaming tests in which similar coal was used.

<sup>c</sup> Alkalies not determined.



## PREPARATION OF ASH.

The coal samples were ground to 60 mesh with a crusher, rolls, and ball mill as described in Technical Paper 8.<sup>a</sup> The 60-mesh material was spread out on shallow, 6-inch, fire-clay roasting dishes, and reduced completely to ash with occasional stirring in a muffle furnace at a temperature not exceeding 750° C. All of the ash was finally put through a 100-mesh screen and thoroughly mixed.

## PREPARATION OF CONES.

Sufficient ash to make the desired number of cones was transferred to an agate mortar, moistened with dextrin solution, and worked into a plastic mass with a spatula or pestle. After the brass mold (fig. 7) had been lubricated with vaseline the plastic material was firmly pressed into it with a knife spatula, and the surface struck off smooth to make a neat, solid triangular pyramid. The cone was then pushed out of the mold by applying a small knife blade at the base. With a little practice and proper lubrication of the mold the cone can be ejected immediately after molding without waiting for the cone to dry; a slight rounding of the bottom groove of the mold greatly facilitates removal of the cone.

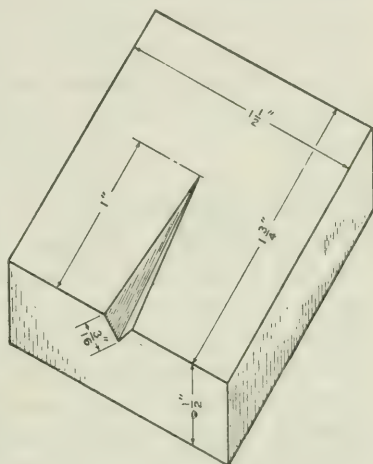


FIGURE 7.—Brass cone mold.

After the cones had dried, they were mounted in a refractory base composed of a mixture of equal parts of kaolin and alumina ( $\text{Al}_2\text{O}_3$ ). This mixture was moistened with water to make it workable, and enough was taken for the base to be made and was spread on a sheet-iron plate. A small hole was made, into which the cone was set, and the base material was worked around the bottom of the cone so that it would be firmly set at the desired inclination in the base. The iron plate was then put on a hot plate, and the mounted cones were dried slowly until all water had been driven off. After the dextrin had been burned by igniting the mounted cones in a muffle, they were ready for use. In the earlier experiments the cones were made directly from the 100-mesh ash; later it was found that ash ground to

<sup>a</sup> Stanton, F. M., and Fieldner, A. C., Methods of analyzing coal and coke: Tech. Paper 8, Bureau of Mines, 1913, pp. 7-9.

an impalpable powder (or at least to pass a 200-mesh screen) made a more substantial and more easily molded cone than 100-mesh material. Four different sizes of cones were used, as follows:

*Sizes of cones.*

- No. 1—Side of base,  $\frac{1}{4}$  inch; height, 1 inch.
- No. 2—Side of base,  $\frac{1}{4}$  inch; height,  $1\frac{1}{2}$  inches.
- No. 3—Side of base,  $\frac{1}{8}$  inch; height, 1 inch.
- No. 4—Side of base,  $\frac{1}{2}$  inch; height,  $2\frac{1}{2}$  inches.

**GENERAL METHOD OF HEATING.**

The general procedure in making a softening-temperature determination was the same with all the furnaces used, though necessarily the details varied in the different furnaces. The test cone was put into the cold or nearly cold furnace and the furnace was heated at the rate of  $10^{\circ}$  to  $15^{\circ}$  C. per minute up to a temperature not less than  $200^{\circ}$  C. below the probable softening point, when the rate (usually  $2^{\circ}$  or  $5^{\circ}$  C. per minute) which had been adopted for that particular determination was begun. Temperature readings were taken every five minutes, and more frequently when the softening temperature was approached. Observations of the appearance of the cone were made at least as often as temperature readings were taken, special care being taken to note any deformation or warping due to shrinking before actual softening began. The point of initial softening or deformation was taken as the temperature at which the first noticeable bending, rounding at the top, or swelling of the cone took place. Warping of the cone due to shrinkage was not considered as the beginning of fusion.

The softening point, deformation point, or "fusion point," so called, was taken as the temperature at which the apex of the cone had bent over to touch the base, or, failing to bend, had fused down to a lump or ball. Sketches (fig. 8) were made of the appearance of the cone at the initial and final deformation points and at several intermediate points of deformation, the corresponding temperatures being noted. Immediately after the temperature corresponding to complete deformation had been read, the current or other source of heat was reduced so that the appearance of the cone could be verified by examination after removal from the furnace.

**TEMPERATURE MEASUREMENTS.**

The temperature measurements were made in two ways, namely, by means of a Heraeus platinum and platinum-rhodium thermocouple with Siemens and Halske high-resistance millivoltmeter, in the platinum-resistance, Meker, and muffle No. 2 furnaces, and the

down-draft ceramic kiln, and by means of a Wanner pyrometer in the molybdenum, carbon-resistance, and Northrup furnaces. The thermocouple and the millivoltmeter were standardized from time to time in the physical laboratory of the bureau under the direction of J. K. Clement, physicist, by comparison with a standard thermocouple. The cold junction was kept at the temperature of melting ice during standardization and during use in measuring temperatures. Further checks on the furnace and the pyrometer were obtained by placing crystals of pure diopside<sup>a</sup> in the positions occupied by the

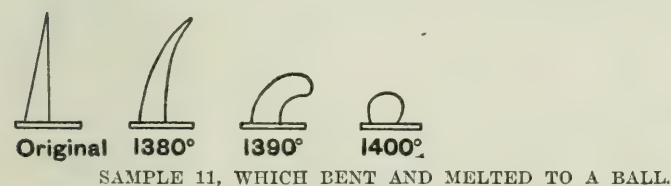
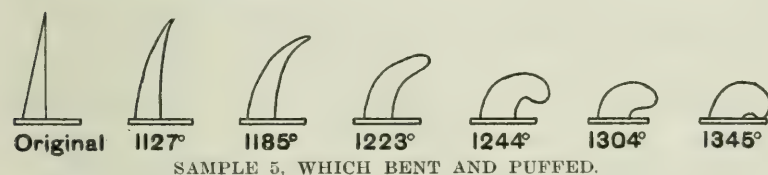
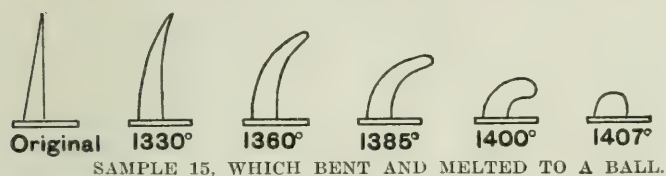
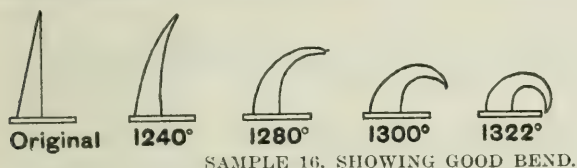


FIGURE 8.—Appearance of ash cones at various stages of softening.

ash cones and noting the temperature of melting; usually the crystal melted between 1,381° and 1,395° C. (corrected temperature readings). The melting point of diopside is 1,391° C.<sup>b</sup>

The Wanner pyrometer which was originally standardized by the Reichsanstalt, was rechecked by the Bureau of Standards after most of the work described in this paper had been completed, and was found to conform to the original standardization. It was checked

<sup>a</sup> Obtained through the kindness of Dr. A. L. Day, director of the Geophysical Laboratory.

<sup>b</sup> Day, A. L., and Sosman, R. B., The melting points of minerals in the light of recent investigations on the gas thermometer: *Am. Jour. Sci.*, vol. 31, 1911, p. 346.



daily against the amyl-acetate flame. As this pyrometer was used only with those furnaces that had strongly reducing atmospheres it was possible to check the accuracy of the pyrometer readings by placing thin strips of Kahlbaum's pure copper or Kahlbaum's pure nickel in place of the cones and noting the apparent melting temperature. This was done at least once a week, and at the beginning and the end of each series of tests.

The results obtained in these checks were usually within 10° C. of the true melting point at the copper point and within 20° C. at the nickel point.

### SUMMARY OF RESULTS OBTAINED IN THE DIFFERENT FURNACES.<sup>a</sup>

#### VARIATIONS DUE TO SIZE AND SHAPE OF CONE.

Three different sizes of cones were compared in the Meker, the carbon-resistance and the molybdenum furnace, namely, cone 1,  $\frac{1}{4}$  by 1 inch; cone 2,  $\frac{1}{4}$ -inch by  $1\frac{1}{2}$  inches; and cone 3,  $\frac{3}{16}$ -inch by 1 inch. The results, which are given in Table 3 following, indicate that cones with a wider base as compared to height, as cone 1, give higher softening temperatures than the more slender cones like cones 2 and 3. In general, the slender type of cone represented by size 3,  $\frac{3}{16}$  by 1 inch, gave shorter softening intervals and less trouble from intumescence due to evolution of gases from the melting ash.

TABLE 3.—Results of tests showing influence of size of cone on softening temperature.

[Rate of heating, 2° C. per minute; 100-mesh ash; cones inclined 35° from vertical.]

Sample No.	Meker furnace.			Carbon furnace.			Molybdenum furnace.		
	Cone 1.	Cone 2.	Difference.	Cone 1.	Cone 2.	Difference.	Cone 1.	Cone 3.	Difference.
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
13.....	1,406	1,273	+133	1,390	1,322	+68	1,217	1,217	0
15.....	1,307	1,186	+121	1,311	1,250	+61	1,167	1,161	+6
16.....	1,225	1,212	+13	1,394	1,341	+53	1,241	1,241	0
17.....	1,242	1,182	+60	1,251	1,220	+31	1,192	1,179	+13
18.....	1,289	1,204	+85	1,316	1,250	+66	1,562	1,558	+4
4.....	1,265	1,305	-40	1,357	1,306	+51	1,227	1,234	-7
5.....	1,388	1,376	+12	1,401	1,356	+45	1,234	1,231	+3
8.....	1,357	1,343	+14	1,192	1,166	+26	1,318	1,263	+55
9.....	1,335	1,318	+17	1,327	1,249	+78	1,213	1,199	+14
1.....				1,100	1,090	+10	1,123	1,123	0
2.....				1,631	1,593	+38	1,430	1,417	+13
3.....				1,558	1,562	-4	1,457	1,396	+61
6.....				1,207	1,179	+28	1,350	1,336	+14
7.....				1,663	1,638	+25	1,590	1,580	+10
10.....				1,187	1,167	+20	1,185	1,192	-7
11.....				1,190	1,139	+51	1,220	1,220	0
12.....				1,088	1,088	0	1,068	1,060	+8
14.....				1,520	1,424	+96	1,326	1,316	+10
Average.....			+46			+41			+11

<sup>a</sup> Complete experimental data and details of furnaces used are given in a previous paper, The fusibility of coal ash in various atmospheres, by A. C. Fieldner and A. E. Hall, Jour. Ind. and Eng. Chem., vol. 7, 1915, pp. 399-406, 474-481.

## INFLUENCE OF FINENESS OF ASH.

Ash ground to an impalpable powder tended to soften at a slightly lower temperature than 100-mesh ash, as is shown in Table 4, following. The difference averaged  $3^{\circ}$  and in no case exceeded  $40^{\circ}$  C. Ash pulverized to at least 200 mesh could be molded into more substantial cones than 100-mesh material.

TABLE 4.—*Influence of fineness of ash on softening temperature.*

[Tests made in molybdenum furnace No. 2;  $\frac{1}{8}$  by 1 inch cone placed in a vertical position; rate of heating,  $\frac{2}{3}$  C. per minute.]

Ash sample No.	Softening point.		Differ- ence.	Ash sample No.	Softening point.		Differ- ence.
	100-mesh.	Impal- pable powder.			100-mesh.	Impal- pable powder.	
	° C.	° C.	° C.		° C.	° C.	° C.
39.....	1,291	1,283	+ 8	67.....	1,223	1,185	+ 38
9.....	1,248	1,304	-56	68.....	1,216	1,205	+ 11
42.....	1,340	1,313	+27	69.....	1,251	1,237	+ 14
48.....	1,380	1,390	-10	70.....	1,259	1,263	- 4
8.....	1,435	1,481	-46	71.....	1,327	1,300	+27
19.....	1,519	1,510	+ 9	72.....	1,368	1,350	+18
2.....	1,492	1,520	-28	73.....	1,380	1,370	+10
64.....	1,108	1,101	+ 7	Average.....			
65.....	1,155	1,127	+28				
66.....	1,174	1,173	+ 1				

## INFLUENCE OF INCLINATION OF CONES.

Mounting the cones with a considerable inclination— $25^{\circ}$  or  $45^{\circ}$  from the vertical—led to premature deformation points in some samples, which were caused by a further bending over due to shrinkage of the cone in its base, rather than deformation due to softening and flowing of the ash. As shown in Table 5, following, differences of  $64^{\circ}$  and  $65^{\circ}$  C. were obtained with two samples. Vertical or nearly vertical cones were free from this source of error and gave the most concordant results.

TABLE 5.—*Influence of inclination of cones on softening temperature.*

[Tests made in molybdenum furnace No. 2; size of cones,  $\frac{1}{8}$  by 1 inch; ash ground to an impalpable powder; rate of heating  $2^{\circ}$  C. per minute.]

Ash sample No.	Softening point.			Difference.	
	Cone inclined $45^{\circ}$ from vertical.	Cone inclined $25^{\circ}$ from vertical.	Cone vertical.	$45^{\circ}$ and vertical.	$25^{\circ}$ and vertical.
	$^{\circ}$ C.	$^{\circ}$ C.	$^{\circ}$ C.	$^{\circ}$ C.	$^{\circ}$ C.
39.....	1,287	1,283	1,283	+ 4	0
42.....	1,295	1,313	1,304	- 9	+9
9.....	1,248	1,304	1,313	-65	-9
33.....	1,396	1,390	1,390	+ 6	0
8.....	1,414	1,481	1,478	-64	+3
19.....	1,494	1,510	1,502	- 8	+8
2.....	1,520	1,520	1,520	0	0
Average.....				-19	+2

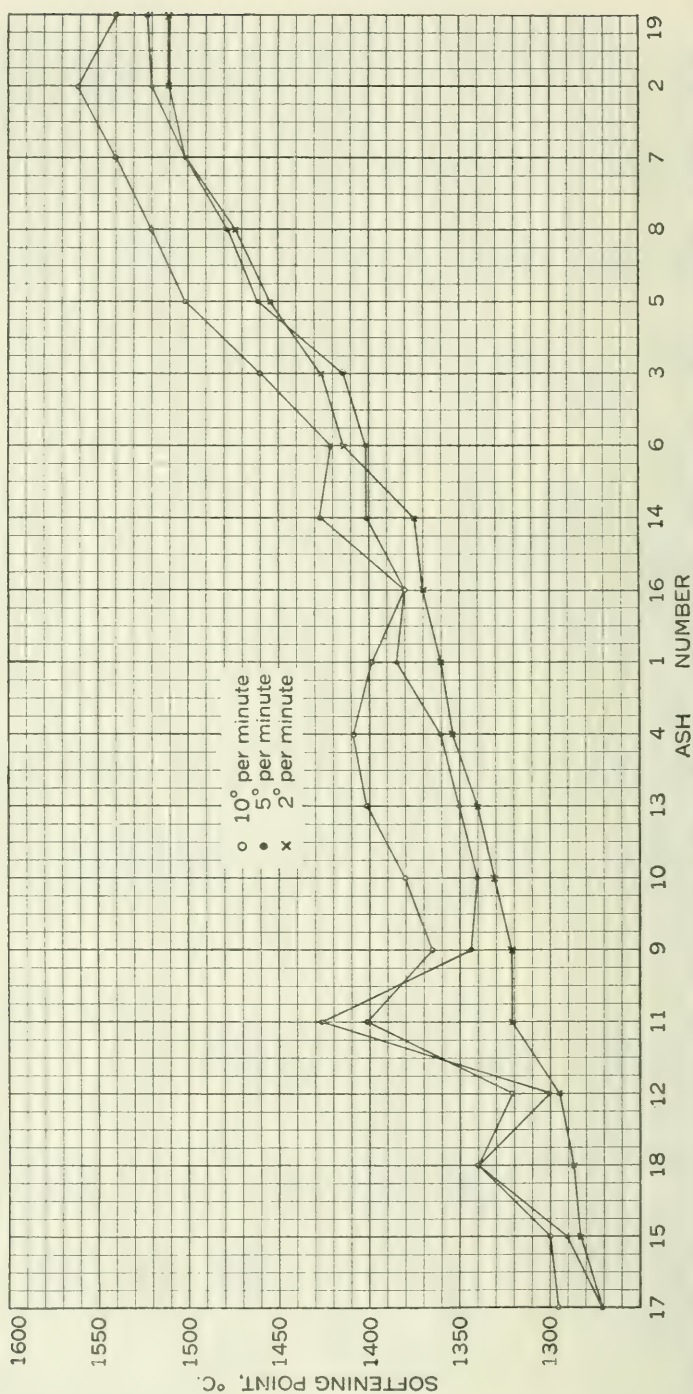


FIGURE 9.—Curves showing results of tests to determine influence of rate of heating on the softening temperature of ash cones in an atmosphere of hydrogen.



## INFLUENCE OF RATE OF HEATING.

As stated previously, the rate of heating has an important bearing on the softening points of silicate mixtures made in the form of Seger cones. The fusion reactions of such mixtures require some time to approach a state of equilibrium. As it was considered probable that these reaction velocities in oxidizing atmospheres would differ from those in reducing atmospheres, tests were made at rates of heating of  $10^{\circ}$ ,  $5^{\circ}$ , and  $2^{\circ}$  C. per minute in an oxidizing atmosphere of air in the platinum furnace, and in a reducing atmosphere of hydrogen in the molybdenum furnace. The softening points obtained are given in figures 9 and 10. These results show that varying the rate of heating from  $2^{\circ}$  to  $10^{\circ}$  C. per minute causes much less increase of softening temperature in oxidizing atmospheres than in reducing atmospheres of hydrogen. This would be expected because of the fact that the melting reactions in hydrogen are further complicated by reducing reactions, all of which are related to the time factor.

It is, of course, desirable to economize time by heating the test specimen as rapidly as is feasible. A safe maximum rate of heating in oxidizing atmospheres seems to be  $10^{\circ}$  C. per minute. However, in reducing atmospheres of hydrogen, several samples when subjected to a temperature rise of even  $5^{\circ}$  C. per minute gave results

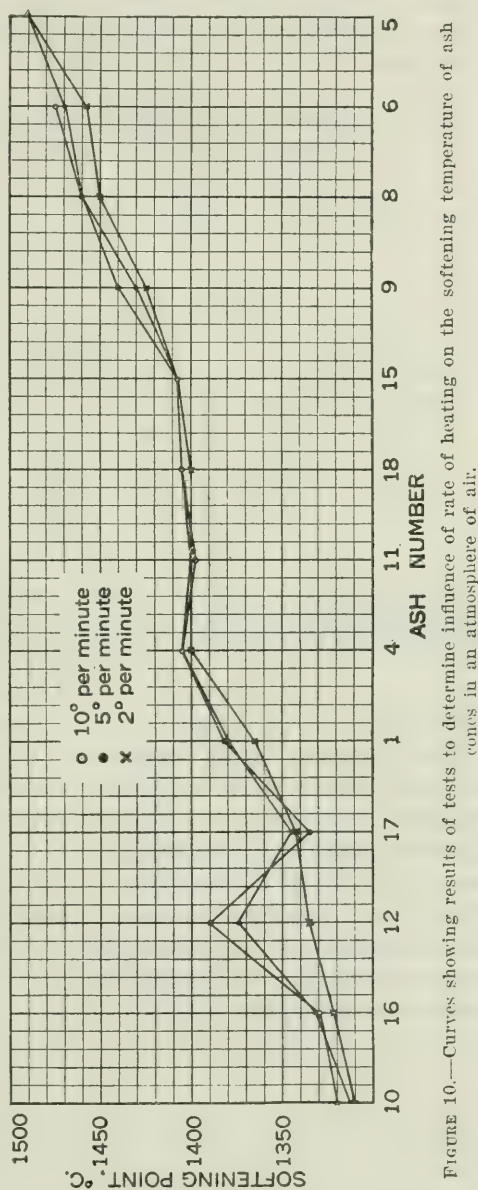


FIGURE 10.—Curves showing results of tests to determine influence of rate of heating on the softening temperature of ash cones in an atmosphere of air.

that were 50° C. higher than when subjected to a rise of 2° C. per minute. Further tests were therefore made in hydrogen, a combined 5° and 2° rate being used. The furnace temperature was increased at the rate of 5° C. per minute until deformation began; the rate was then reduced to 2° C. per minute until the cone was down. As shown by Table 6, the results approximated those obtained with the usual rate of 2° C.

TABLE 6.—*Results of tests showing comparative softening temperatures in molybdenum furnace No. 2 at two different rates of heating.*

[Ash ground to an impalpable powder; cone,  $\frac{3}{8}$  by 1 inch, placed in a vertical position.]

Ash sample No.	Softening point.		Difference.
	Temperature rise of 2° C. per minute. <sup>a</sup>	Temperature rise of 5° and 2° C. per minute. <sup>b</sup>	
	° C.	° C.	° C.
58.....	1,199	1,220	-21
50.....	1,220	1,217	+ 3
49.....	1,520	1,514	+ 6
55.....	1,380	1,370	+10
28.....	1,390	1,394	- 4
52.....	1,448	1,478	-30
61.....	1,365	1,370	- 5
Average.....			- 6

<sup>a</sup> Furnace temperature was increased at the rate of 2° C. per minute until cone was down.

<sup>b</sup> Furnace temperature was increased at the rate of 5° C. per minute until deformation began; the rate was then reduced to 2° C. per minute until the cone was down.

#### INFLUENCE OF DEXTRIN BINDER.

The results of a few experiments made to show the effect of not burning out the dextrin binder before placing the ash cone in the molybdenum furnace are given in Table 7 following. The maximum apparent effect was a lowering of 11° C. in the softening point. Mixing 10 per cent of dry dextrin with the ash caused a reduction of only 14° C. However, the conclusion that dextrin causes no material effect would apply only under the conditions of determining the softening point in hydrogen and water-vapor mixtures as was done in the experiments mentioned.

TABLE 7.—*Results of experiments to determine influence of dextrin binder on softening temperature of ash cones.*

[Test made in molybdenum furnace No. 2; cones  $\frac{1}{8}$  in. by 1 inch, inclined 35° from vertical; 100-mesh ash; rate of increase of heating 2° C. per minute.]

Ash sample No.	Softening point.		Difference.
	Dextrin binder not ignited.	Dextrin binder ignited.	
	° C.	° C.	° C.
2.....	1,492	1,502	-10
8.....	1,435	1,434	+ 1
12.....	1,260	1,271	-11
8.....	1,430	1,434	- 4
Average.....	.....	.....	- 6

## INFLUENCE OF DIFFERENT CONDITIONS ON SOFTENING POINT OF ASH SAMPLE 8.

Conditions.	Softening point, °C.
Cone made in usual manner, then ignited in air at 850° C. ....	1,434
1 per cent dry dextrin mixed with the ash; dextrin not ignited--	1,427
10 per cent dry dextrin mixed with the ash; dextrin not ignited -----	1,420

## INFLUENCE OF VARIOUS ATMOSPHERES.

None of the various factors affecting softening temperatures that have thus far been discussed seems capable of causing the exceedingly large differences in softening temperature that have been reported from different laboratories with the same samples of ash. For instance, Marks <sup>a</sup> has called attention to differences as great as 390° C. that were obtained with the same sample of ash by two different commercial laboratories. He himself obtained differences of 200° C. with some duplicate samples that were tested in a Meker muffle furnace and a Hoskins graphite electric furnace. As stated by Marks, these large differences were undoubtedly due to the oxidizing or reducing action of the respective furnace atmospheres. It was realized at the outset of the investigation described in this report that the reaction of the furnace gases with the iron constituent of the ash would largely determine the softening temperature. Therefore, comparative tests were made in the six different furnaces previously described in order to show the effect of various oxidizing and reducing atmospheres.

The first series of oxidizing-atmosphere tests was made in an atmosphere of air in a platinum resistance furnace (fig. 2, p. 22), in which there could be no trace of reducing gases. The second series of tests was made in a gas-heated Meker muffle furnace (fig. 3, p. 22), and

<sup>a</sup> Marks, L. S., The clinkering of coal: Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 205-214.



the third series in a fire-clay gas muffle-furnace. As shown in figure 11, the platinum-furnace results were higher than those obtained in the gas furnaces. There was evidence of reduction by products of incomplete combustion from the fuel gases surrounding the muffles. The reduction was seemingly greater in the muffle furnace than in the gas furnaces. There was evidence of reduction by products of incom-

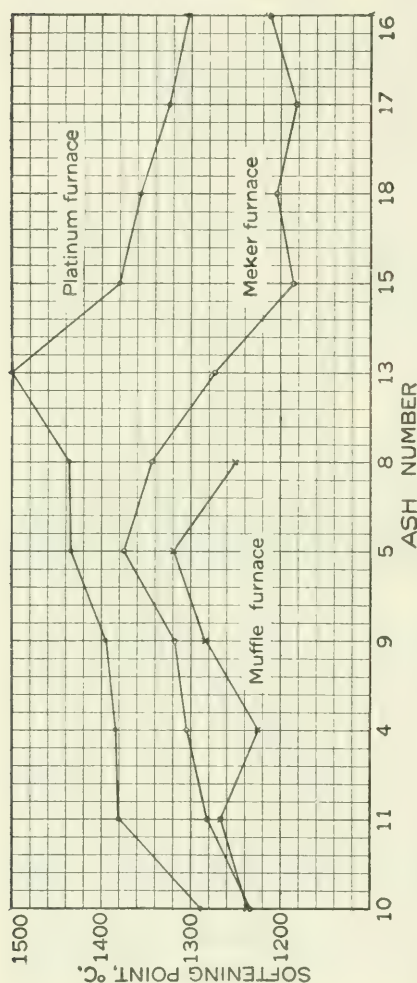


FIGURE 11.—Curves showing results of tests to determine softening temperatures in Meker furnace, muffle furnace No. 2, and platinum furnace.

plete combustion from the fuel gases surrounding the muffles. The reduction was seemingly greater in the muffle furnace than in the Meker furnace, probably because the muffle furnace contained a rather porous fire-clay muffle, whereas the Meker furnace contained a special refractory muffle of dense texture.

From these results it is evident that softening-temperature tests made in gas furnaces must be made with the furnace operated under definite oxidizing or reducing conditions if duplicate results are to be obtained.

In the tests made in the gas furnaces there was evidence of some reduction of ferric iron to the ferrous form, but not to metallic iron. To show the effect of strongly reducing atmospheres such as would cause the formation of metallic iron, tests were made in a granular-carbon resistance furnace (fig. 5, p. 24) and a Northrup graphite furnace

(fig. 6, p. 25), both having atmosphere of carbon monoxide (CO), and in a molybdenum resistance furnace (fig. 4, p. 23) having an atmosphere of hydrogen. The results obtained in the carbon, the Northrup, and the platinum furnaces are given in figure 12. As would be expected, the strongly reducing atmosphere of carbon monoxide completely changes the softening characteristics of the ash,

so that results widely different from those found in the platinum furnace in air were obtained.

As both the Northrup and the granular-carbon resistance furnace produced atmospheres of carbon monoxide, similar softening temperatures were expected in the two series; that such did not prove to be the result is shown in figure 12. In 16 of 18 samples tested, the softening points in the Northrup furnace were higher than in the carbon furnace; the maximum was  $396^{\circ}$  C. and the average difference for the series was  $134^{\circ}$  C. The checks made on materials of known melting points, at various times during the course of these experiments, effectually rule out the possibility of attributing these large differences of temperature measurement. The only explanation offered by the authors is that in the carbon furnace the reduction of ferric oxide to metallic iron did not proceed as rapidly or as completely as in the Northrup furnace; in the latter the ash cone is heated in a closed tube of graphite, practically all air being excluded, so that only nitrogen, carbon monoxide (CO), and a fractional percentage of carbon dioxide ( $\text{CO}_2$ ) surrounds the ash at temperatures above  $1,100^{\circ}$  C. Such an atmosphere would reduce the ferric oxide to metallic iron and thus prevent the formation of a low-melting ferrous silicate eutectic. On the other hand, the carbon furnace had an alundum tube between the carbon resistor and the cone, and it also permitted air to leak into the heating space as shown by the appearance of carbon monoxide flames at the peephole and around the cover plate. Sufficient carbon dioxide may therefore have been present to retard the reduction to metallic iron, thus leaving enough of the strongly fluxing ferrous oxide in the ash to form a low-melting fluid eutectic which caused the cone to collapse at a comparatively low temperature. Examination of polished sections of fused cones from both furnaces disclosed more metallic iron in those from the Northrup furnace.

Figure 13 shows the results obtained in the series of tests in the hydrogen atmosphere of the molybdenum furnace as compared with the results of the tests in the platinum and the Northrup furnaces. It is quite evident that the softening temperature in hydrogen is different from that in air or carbon monoxide.

The softening temperatures obtained in the six different furnaces are given in Table 8 following. The maximum differences range from  $134^{\circ}$  to  $396^{\circ}$  C. As regards 14 samples that softened below  $1,500^{\circ}$  C. in the platinum furnace in air, 9 gave their highest results in the strongly reducing carbon monoxide atmosphere of the Northrup furnace (see fig. 12); and 5 gave their highest results in the oxidizing atmosphere of the platinum furnace. The lowest softening points in 18 samples were distributed among the different furnaces as fol-

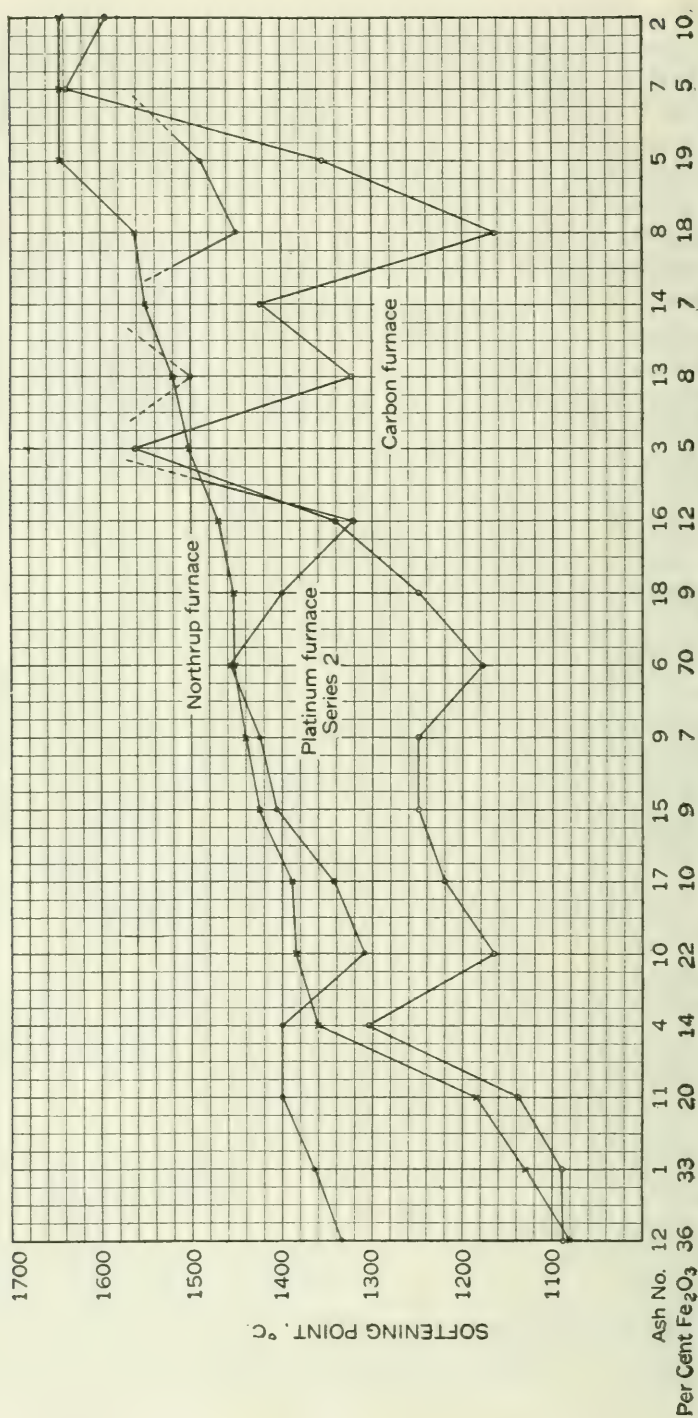
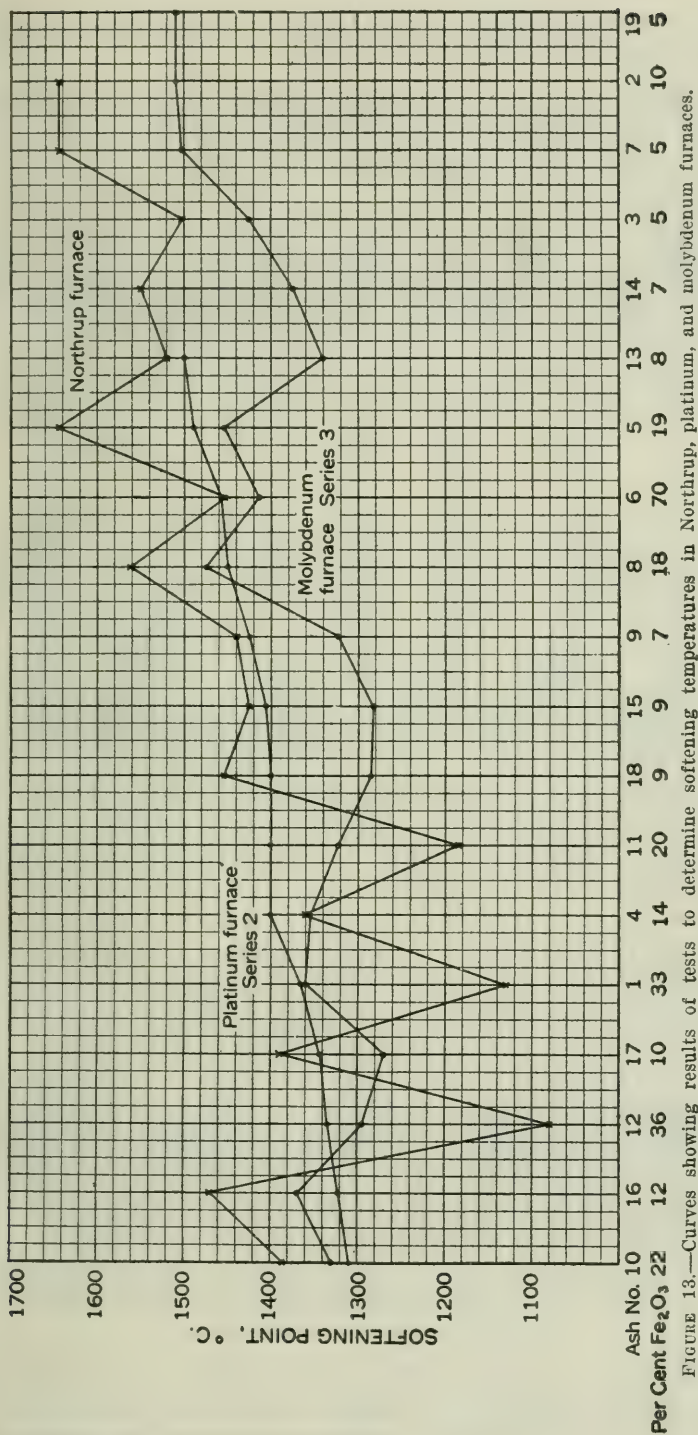


FIGURE 12.—Curves showing results of tests to determine softening temperatures in Northrup, carbon-resistance, and platinum furnaces.





lows: Carbon furnace, 6; Meker furnace, 5; molybdenum furnace, 4; muffle furnace, 2; Northrup furnace, 1.

TABLE 8.—*Results of tests to determine influence of various atmospheres on softening temperatures of ash cones in different furnaces.*

[Rate of heating, 2° C. per minute.]

Ash sample No.	Softening point.						Maximum difference.
	Northrup furnace, <i>a</i> in atmosphere of CO+N.	Carbon furnace, <i>b</i> in atmosphere of CO+CO <sub>2</sub> +N.	Molybdenum furnace, <i>b</i> in atmosphere of H.	Muffle furnace, <i>b</i> in atmosphere of air+combustion gases.	Meker furnace, <i>b</i> in atmosphere of air+combustion gases.	Platinum furnace, <i>a</i> in atmosphere of air.	
	° C.	° C.	° C.	° C.	° C.	° C.	° C.
1.....	1,131	1,090	1,360	1,192		1,365	275
2.....	1,645	1,593	1,511			Above 1,500	134
3.....	1,502	1,562	1,427			Above 1,500	135
4.....	1,360	1,306	1,355	1,226	1,305	1,400	174
5.....	1,645	1,356	1,455	1,320	1,376	1,490	325
6.....	1,455	1,179	1,414	1,318		1,458	279
7.....	1,645	1,638	1,502			Above 1,500	143
8.....	1,562	1,166	1,474	1,251	1,343	1,450	396
9.....	1,440	1,249	1,322	1,284	1,318	1,425	191
10.....	1,385	1,167	1,331	1,199		1,310	218
11.....	1,185	1,139	1,322	1,214		1,400	261
12.....	1,080	1,088	1,295	1,182		1,335	255
13.....	1,520	1,322	1,340		1,273	1,500	247
14.....	1,551	1,424	1,375		1,417	Above 1,500	176
15.....	1,427	1,250	1,283		1,186	1,407	241
16.....	1,470	1,341	1,370		1,212	1,322	258
17.....	1,390	1,220	1,271		1,182	1,343	208
18.....	1,455	1,250	1,287		1,204	1,400	251

*a* Ash ground to an impalpable powder; cones  $\frac{3}{8}$  by 1 inch, placed in vertical position.

*b* Ash 100 mesh; cones  $\frac{1}{2}$  inch by  $1\frac{1}{2}$  inches, inclined 35° from vertical.

There seems to be no consistent relation between the results obtained in the different furnace atmospheres. Some ashes have a higher softening point in an oxidizing atmosphere; others in a reducing atmosphere of carbon monoxide. The only general conclusion that can be made regarding the effect of the atmosphere is that a given ash will have its highest temperature of softening in either an atmosphere of air, free from all traces of reducing gases, or in a strongly reducing atmosphere in which the concentration of reducing gases is so great that the iron constituents of the ash are largely reduced to the metallic form. Between these two extremes of oxidation and reduction, there seems to be a condition of slight reduction by mixed gases such as was found in the muffle furnaces, in which reduction of ferric oxide proceeded until the oxide was largely in the ferrous state. On account of its strongly fluxing action ferrous oxide greatly lowers the temperature of slag formation.

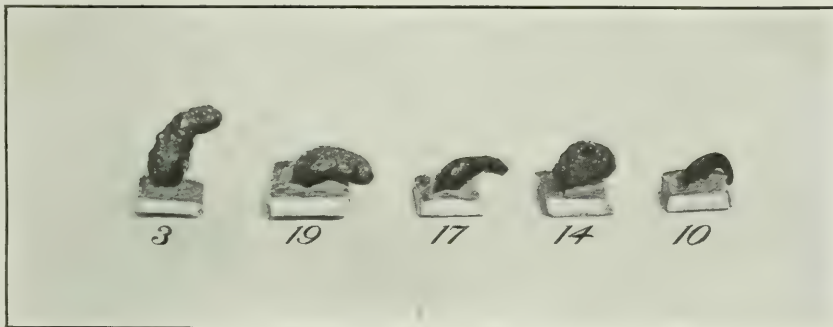
#### APPEARANCE OF CONES SOFTENED IN VARIOUS ATMOSPHERES.

##### PLATINUM FURNACE, ATMOSPHERE OF AIR.

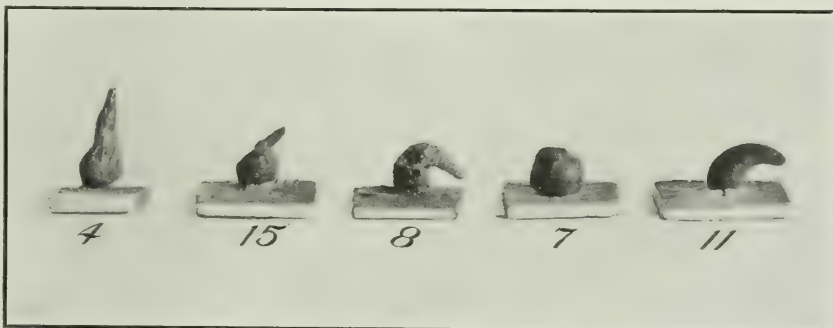
In Plate I, *A*, are shown the various shapes into which cones of different ashes deform when heated in air in the platinum furnace. The manner of deformation is somewhat characteristic for each indi-



A. TYPICAL FORMS OF CONES FUSED IN AIR IN THE PLATINUM FURNACE.



B. TYPICAL FORMS OF CONES FUSED IN HYDROGEN IN THE MOLYBDENUM FURNACE.



C. TYPICAL FORMS OF CONES FUSED IN CARBON MONOXIDE IN THE NORTHRUP FURNACE.





vidual ash. No. 59 illustrates the typical form of bending of Seger cones; No. 26 illustrates the type that fuses to a lump; No. 29 is representative of the intumescent type; No. 7 is an ash which did not soften at 1,500°. The color of the fused cones varied from a buff, or reddish brown, to a glossy black. The black cones were magnetic.

MOLYBDENUM FURNACE, ATMOSPHERE OF HYDROGEN.

Plate I, *B*, illustrates typical forms from the molybdenum furnace (hydrogen atmosphere). Owing to the reducing atmosphere, these cones almost always developed a pronounced vesicular structure. The swelling due to the evolution of gas in some cones, as in ash No. 3, prevented the cones from bending in the normal manner. This is one of the reasons for the somewhat larger variations between duplicate determinations in reducing atmospheres. The fused cones were usually light to dark gray or grayish black; they had a vitreous luster and invariably showed iron globules when examined under the microscope.

NORTHROP FURNACE, ATMOSPHERE OF CARBON MONOXIDE AND NITROGEN.

The cones fused in the Northrup furnace (Pl. I, *C*) (CO atmosphere) varied from a dark-gray to a brownish-black or metallic-black color. The surface lacked the vitreous luster of the cones fused in air or hydrogen. Carbon was deposited on the cones and the bases under the cones in increasing quantity as the temperature exceeded 1,400° C., as shown by the blackened base of ash No. 8 (Pl. I, *C*), which was heated to 1,550° C.

Another peculiarity in the cones tested in the Northrup furnace was the softening and swelling of the thick bottom parts of some of the cones before the apexes began to soften. Ash No. 4 began swelling at the base at 1,200° C.; heating was continued at a temperature increase of 2° C. per minute until a temperature of 1,375° C. was reached, when the current was interrupted and the furnace allowed to cool. As shown in Plate I, *C*, fusible constituents appeared to separate and run down the sides of each cone, leaving a refractory skeleton standing. However, when the cone was broken, the irregular contour appeared to be due to the evolution and expansion of gases in the interior of the softening slag. The expanded bottom was a thin-shelled bubble of slag.

The first perceptible swelling of the lower part of ash No. 8 took place at 392° C. below the temperature at which it finally bent over in the position shown in Plate I, *C*.

The earlier fusion of the thick part of the cone may be due to the inability of the carbon monoxide to penetrate and reduce to metallic iron the iron oxide in the interior as rapidly as in the thin upper part. This phenomenon of irregular softening was noted only in the Northrup and the carbon-resistance furnaces.

## STANDARD METHODS FOR DETERMINING SOFTENING TEMPERATURE OF ASH.

A standard method for determining the softening temperature of ash may now be considered. Obviously, the statement that an ash has a "fusing" or softening temperature of  $1,500^{\circ}\text{C}$ . means nothing unless the exact conditions of making the test are defined. The method must therefore be carefully standardized in all its details before directly comparable results may be obtained by different workers.

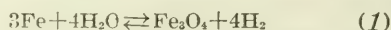
The most important consideration is the atmosphere in which the test shall be made. In order to obtain results that can be duplicated in different laboratories, the softening temperature in air, as was determined in the platinum furnace, is undoubtedly the most satisfactory method, but, unfortunately, ash forming in a fuel bed is not free from the effect of reducing gases. Consequently, clinkering may take place under conditions of partial reduction similar to those that prevailed when the low softening points were obtained in the experiments described. Therefore the danger point as regards clinker formation is the lowest possible softening temperature of an ash under such conditions of reduction as are probable in a fuel bed.

The problem resolves itself into an investigation of the effects of various mixtures of a reducing gas and its product of oxidation on the softening temperature with a view to finding that mixture which will give the lowest softening temperature. The two principal reducing gases to be considered are hydrogen and carbon monoxide, the respective oxidation products being water and carbon dioxide.

## FUSIBILITY OF COAL ASH IN MIXTURES OF HYDROGEN AND WATER VAPOR.

### THEORETICAL CONSIDERATIONS.

The equilibrium between hydrogen, water vapor, Fe, and  $\text{Fe}_3\text{O}_4$  according to the reaction,



was first studied by Deville<sup>a</sup> at various temperatures between  $200^{\circ}$  and  $1,000^{\circ}\text{C}$ ., and later with greater precision by Preuner<sup>b</sup> at three temperatures. Preuner found the following mean values for the equilibrium constant:

<sup>a</sup> Deville, H. Sainte-Claire, *Action de l'eau sur le fer et le hydrogène sur l'oxyde de fer*: *Compt. rend.*, t. 70, 1870, pp. 1105-1111 and 1201-1205.

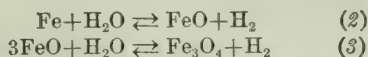
<sup>b</sup> Preuner, G., *Das Gleichgewicht zwischen Eisen, Eisenoxyduloxyd, Wasserstoff, und Wasserdampf*: *Ztschr. phys. Chem.*, Bd. 47, 1904, pp. 385-417.



*Equilibrium data of Preuner.*

Temperature of solid phase, °C.	$p_{H_2O}$ .
900 -----	0.69
1025-1050 -----	.78
1150 -----	.86

Chaudron<sup>a</sup> has since reported two series of equilibria of iron and its oxides in hydrogen and water vapor corresponding to the following reactions:



His values for the equilibrium constants are as follows:

*Equilibrium data of Chaudron.*

Reaction 2.		Reaction 3.	
Temperature of solid phase.	$\frac{p_{H_2O}}{p_{H_2}}$	Temperature of solid phase.	$\frac{p_{H_2O}}{p_{H_2}}$
°C.		°C	
360	0.12	440	0.24
440	.18	480	.32
500	.23	500	.33
550	.32	615	.54
600	.31	700	1.00
630	.36	710	1.00
660	.39	800	1.35
760	.55	860	2.00
875	.74		

No similar data are available on the behavior of ferric oxide ( $\text{Fe}_2\text{O}_3$ ); hence these data for magnetite include the only available information as to the probable or possible phases in which the iron oxide of coal ash may exist in various mixtures of hydrogen and water vapor at the sintering temperature of ash.<sup>b</sup>

In figure 14 are plotted the equilibrium data of Preuner and of Chaudron. Assuming that  $\text{Fe}_2\text{O}_3$  reacts as regards reduction in a similar manner as does  $\text{Fe}_3\text{O}_4$ , it is evident that at temperatures up to 1,150° C. no reduction to metallic iron can take place in a mixture of equal parts by volume of hydrogen and water vapor. At a temperature of 850° C., according to Chaudron's figures, FeO would be the stable solid phase in mixtures containing not less than 43 or more than 63 per cent of water vapor, it being assumed that a gas mixture of constant composition is passed over the heated oxide continuously, sweeping the gaseous products of the reaction out of the apparatus.

<sup>a</sup> Chaudron, G., Réactions réversibles de l'eau sur le fer et sur l'oxyde ferreux: *Compt. rend.*, t. 159, 1914, pp. 237-239.

<sup>b</sup> Recent investigations by Sosman and his coworkers at the geophysical laboratory have shown that the equilibrium relationships of the iron oxides are further complicated by solid solution. In the system  $\text{Fe}_2\text{O}_3$ - $\text{Fe}_3\text{O}_4$  there is a continuous solid solution series from  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ .

It seems possible, therefore, that a minimum softening temperature of coal ash may be found in a mixture approximating equal parts by volume of hydrogen and water vapor, provided the heating is sufficiently slow to allow the reaction to approach equilibrium at the various temperatures.

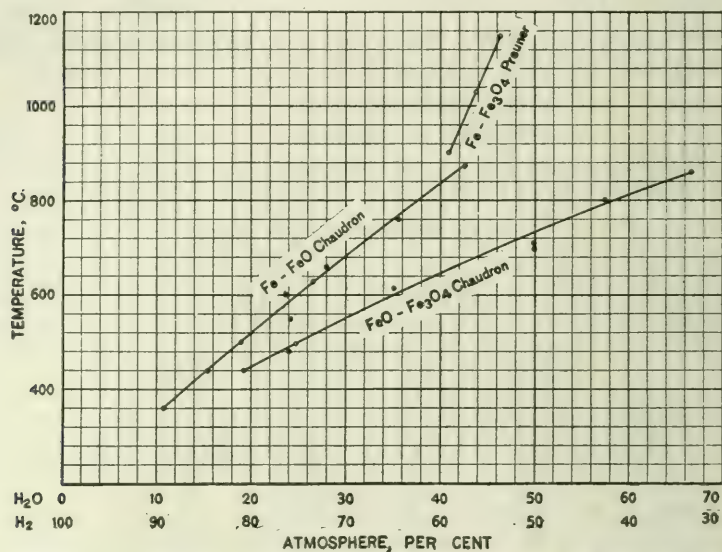


FIGURE 14.—Equilibrium diagram of the system  $\text{H}_2$ ,  $\text{H}_2\text{O}$ , Fe, FeO, and  $\text{Fe}_3\text{O}_4$ .

## OUTLINE OF EXPERIMENTS.

### DESCRIPTION OF FURNACE.

The arrangement of the furnace and of the saturator used in the authors' tests is shown in Plate II, and figures 15 and 16. A Heræus

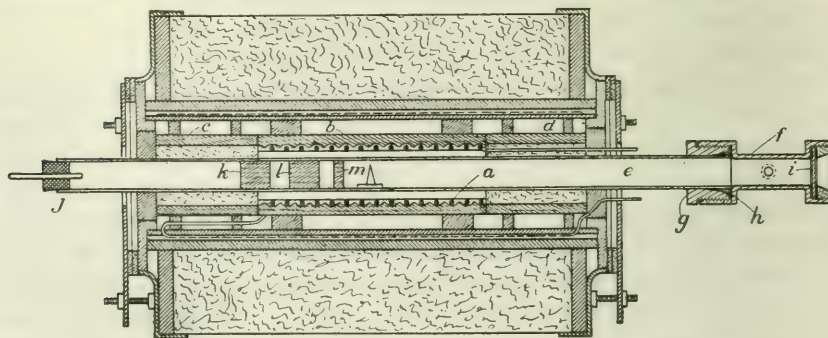
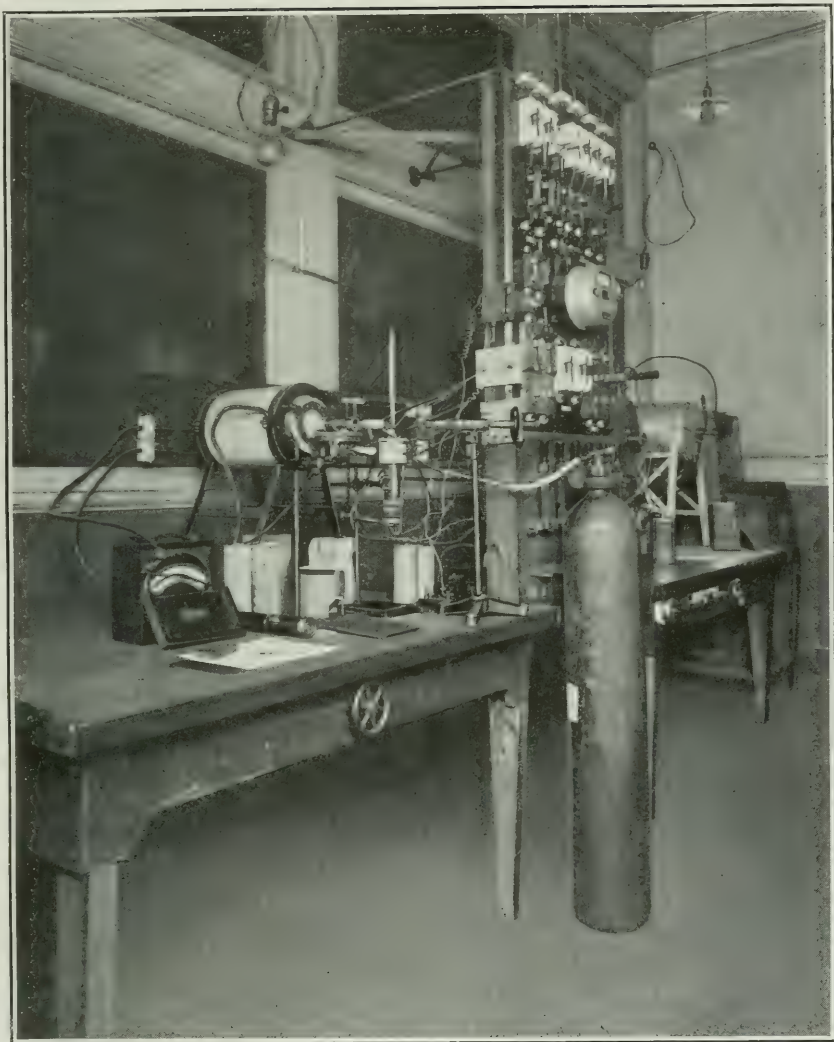


FIGURE 15.—Vertical longitudinal section through silica-tube furnace.

platinum-foil resistance furnace which happened to be available was equipped with an extra heater of  $\frac{3}{100}$ -inch platinum wire, *a* (fig. 15),



ARRANGEMENT OF SILICA-TUBE FURNACE AND ACCESSORIES.





wound on the inside of the alundum tube *b*, and connected in series with the platinum-foil<sup>a</sup> heating unit of the Heræus furnace.

This alundum heater tube was supported on two alundum rings, leaving a  $\frac{1}{2}$ -inch air space between the heater tube and the Heræus

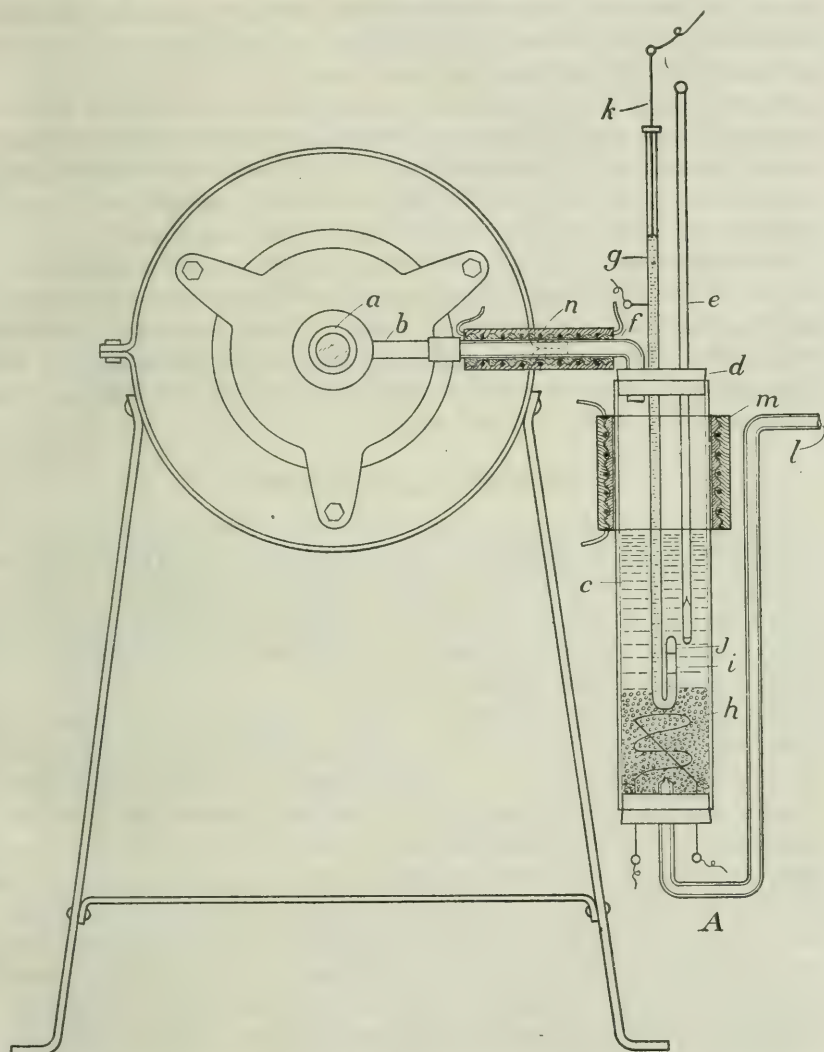


FIGURE 16.—Front elevation of silica-tube furnace and vertical section through saturator.

porcelain tube. Two additional alundum tubes, *c* and *d*, were placed similarly, one at each end of the platinum-wound tube. Through the furnace, modified in this way, was passed a tube *e*, of fused silica, glazed on both sides, five-eighths inch in inside diameter and 17 inches long.

<sup>a</sup> A nichrome heating element could as well be used for the outer heating unit.

The gas mixture entered the silica tube through the brass end piece *f*, which was specially designed to make a gas-tight connection by means of the brass bushing *g* and the asbestos packing *h*. A removable glass window, *i*, permitted removal and insertion of cones in the furnace, and observation of deformation and of temperature with the optical pyrometer. The glass was held in place between asbestos washers by a threaded brass ring.

An air bath was placed around the end piece *f* to maintain its temperature above 100° C., and thus avoid any condensation of water vapor; the exit end *g* was made sufficiently short so that its temperature should be above 100° C. The gas mixture passed out through the glass capillary tube inserted in the rubber stopper at *j*.

Alundum stops, *k*, *l*, and *m*, were placed at intervals back of the middle of the inner heater to provide a suitable background for taking readings with the optical pyrometer. These stops were made of thin-walled alundum tubes closed at one end, fitting snugly in the silica tube. To avoid rapid devitrification of the fused-silica tube, temperatures were not carried above 1,400° C.

#### DESCRIPTION OF "SATURATOR."

The apparatus by which various mixtures of hydrogen and water vapor were formed depended on the saturation of pure hydrogen gas with water vapor at temperatures ranging from zero to within a degree or two of the boiling point. It is shown in figure 16 with furnace connections as used, except the hot-air bath surrounding the brass end piece *a*, and the side tube *b*.

The saturator consists of a glass tube *c*, 1 $\frac{3}{4}$  inches in diameter and 9 inches long, closed at the ends with rubber stoppers. Through the upper stopper *d* passes the thermometer *e*, the outlet tube *f* communicating with the furnace through the brass tube *b*, and a compact adjustable vapor-pressure thermoregulator *g*, with electrical connections controlling through a relay the current in the heating coil *h*. The thermoregulator is essentially that described by Feild,<sup>a</sup> without the refinement of being independent of atmospheric pressure. It consists of a bent-glass tube, in the short arm of which is a small volume of liquid *i*—ether, alcohol, or water, depending on the temperature desired—resting on a mercury column. Above the liquid *i*, is a small volume of its saturated vapor *j*, the pressure of which depends only on the temperature and determines the height of the mercury column. This mercury column makes and breaks contact with the platinum wire *k*. The temperature control, with a continuous stream of hydrogen bubbling around the glass beads *h* and

<sup>a</sup> Feild, A. L., An electrical-contact vapor-pressure thermoregulator: Jour. Am. Chem. Soc., vol. 36, 1914, pp. 72-76.



through the water *c* was within  $0.1^{\circ}$  to  $0.2^{\circ}$  C., which was sufficiently accurate for the purpose of the experiments. Hydrogen stored in a high-pressure cylinder was introduced at *l*, and its flow so adjusted as to give the desired current of hydrogen and water vapor through the fused-silica furnace tube. The water vapor present in the mixture of hydrogen and water vapor was prevented from condensing to liquid water on its passage to the furnace by two heating coils *m* and *n*, constructed of nichrome wire wound on alundum cores and heated, similarly to the immersed coil *h*, by a current from a low-voltage transformer operating at about 11 volts. An air-bath chamber of asbestos paper, heated by a small electric hot plate, was placed around the brass end piece *a* and the side tube *b*.

Analyses were made of the mixtures of gas and water vapor issuing from the end of the silica tube. With the saturator adjusted for a mixture containing 50 per cent of each, 52 per cent hydrogen and 48 per cent water vapor were found; adjusting for an atmosphere of 89 per cent water vapor, 91 per cent was found. This degree of accuracy was considered satisfactory.

#### PREPARATION OF TEST PIECE.

The ash ground to 200 mesh was molded with the aid of dextrin solution into a slender triangular pyramid or Seger cone and mounted, with one side vertical, in a refractory base, according to the method previously described. On account of the small diameter of the fused-silica tube, it was possible to use only the upper half of the standard three-sixteenth by 1 inch cone adopted in the former experiments. Before the cone was placed in the furnace the dextrin binder was burned off by ignition at a red heat in a muffle.

#### MEASUREMENT OF TEMPERATURE.

The temperatures were read with a Wanner optical pyrometer, which was sighted on the thin alundum disk just back of the cone. A correction for absorption by the glass window was made.

The pyrometer was compared daily with the standard amyl-acetate flame, and once each week a thin piece of Kahlbaum's pure copper foil was substituted for the ash cone and its melting point read in an atmosphere of hydrogen. The results were between  $1,075^{\circ}$  and  $1,090^{\circ}$  C. (melting point,  $1,083^{\circ}$  C.).

#### RESULTS OF EXPERIMENTS.

Softening-temperature determinations were made with five different samples of coal ash (see Tables 1 and 2, pp. 26 and 27) containing

7 to 69 per cent of ferric oxide ( $\text{Fe}_2\text{O}_3$ ), in various atmospheres ranging from pure dry hydrogen to pure water vapor. The temperature was raised at the rate of  $10^\circ$  to  $15^\circ$  C. per minute to approximately  $900^\circ$  C.; it was then raised  $5^\circ$  C. per minute until deformation began, and  $2^\circ$  C. per minute thereafter until the cone was down. The dry hydrogen was obtained by bubbling the hydrogen through a wash bottle of concentrated sulphuric acid. The 100 per cent water-vapor atmosphere was obtained by cutting off the hydrogen from the saturator and heating the water to boiling.

All the results obtained are given in Table 9 following, in which the softening temperature is given as a temperature interval, the lower figure being the temperature at which deformation (rounding of the apex or bending of the cone) began, and the higher figure being the temperature at which the cone bent so that the apex touched the base, or, failing to bend, softened to a lump. This latter final deformation point is meant when reference is made to the "fusion," "softening," or "deformation" point of an ash.

TABLE 9.—Results of experiments to determine softening temperatures of ash in various mixtures of hydrogen and water vapor.

Laboratory No.....	15848	16586	15844	16243	15845
Percentage of $\text{Fe}_2\text{O}_3$ ..	7.0	11.8	19.0	35.9	69.7
Percentage of $\text{H}_2\text{O}$ in atmosphere.	Softening temperature.				
	$^\circ\text{C.}$	$^\circ\text{C.}$	$^\circ\text{C.}$	$^\circ\text{C.}$	$^\circ\text{C.}$
0.0.....	1,322-1,360	1,390-1,402	Above 1,400	1,304-1,370	Above 1,400
0.7.....				1,331-1,355	
5.7.....	1,279-1,290	1,313-1,360	Above 4,000		Above 1,400
6.3.....				1,248-1,263	
7.6.....				1,220-1,270	
10.7.....			<sup>a</sup> 1,340		
12.4.....		1,279-1,313	1,155-1,271		
15.8.....					1,304-1,330
18.1.....				1,104-1,198	
19.9.....			1,173-1,271		
29.6.....				1,056-1,064	
31.2.....	1,179-1,271	1,227-1,251	1,173-1,263		1,227-1,322
41.7.....				1,048-1,062	
51.2.....				1,072-1,078	
57.5.....	1,220-1,292	1,220-1,258	1,173-1,255		1,104-1,322
77.2.....				<sup>a</sup> 1,095	
83.2.....				<sup>a</sup> 1,095	
83.9.....	1,173-1,295	1,241-1,249	1,227-1,263		1,206-1,350
90.3.....		1,227-1,251	1,206-1,295	<sup>a</sup> 1,095	
94.8.....				1,048-1,080	
100.0.....	1,350-1,370	1,313-1,322	Above 1,400	1,304-1,313	Above 1,402

<sup>a</sup> Temperature at end of deformation of cone; temperature at which deformation began not observed.

The final deformation points are plotted in figure 17, in which the abscissas represent the percentages of water vapor in the mixture, and the ordinates the temperatures of final deformation. The initial deformation points are plotted in a similar manner in figure 18.

It will be noted that both sets of curves have well-defined minima when the water vapor formed 40 to 70 per cent of the atmosphere.

The final deformation points (fig. 17), which were more accurately determined, show a fairly uniform minimum in mixtures ranging from 30 to 70 per cent water vapor. The establishment of this relation enables the formulation of a practical method of determining

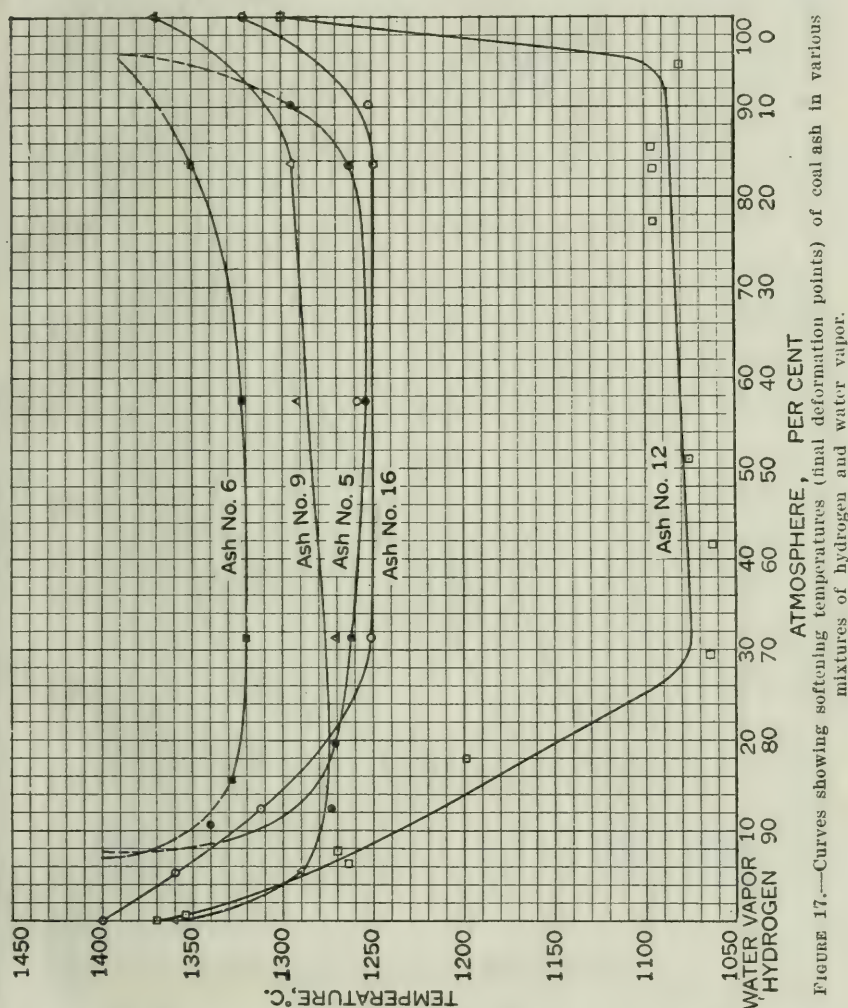


FIGURE 17.—Curves showing softening temperatures (final deformation points) of coal ash in various mixtures of hydrogen and water vapor.

the lowest softening temperature of an ash in a mixture of approximately equal parts of hydrogen and water vapor. Seemingly, the gas mixture need only be controlled between limits of 30 and 70 per cent water vapor to insure the lowest softening temperature of the ash, within the unavoidable experimental deviation in determinations of this character.



The pronounced effect of viscosity on the rate of deformation of the ash cones is shown in the relative positions of the curves of initial deformation in figure 18 and the curves of final deformation in figure 17. Sample 16586 had the highest initial-deformation temperature

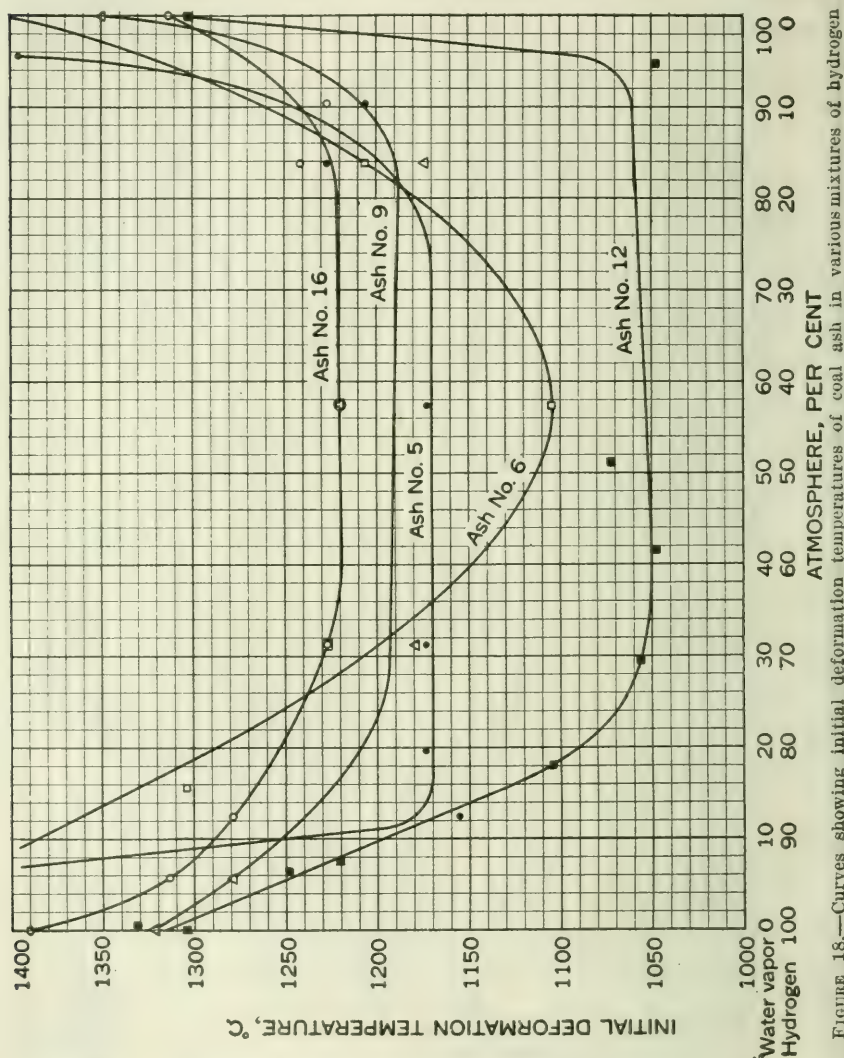


FIGURE 18.—Curves showing initial deformation temperatures of coal ash in various mixtures of hydrogen

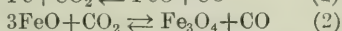
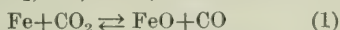
and next to the lowest final-deformation temperature in an atmosphere containing equal parts of hydrogen and water vapor. This was due to the low viscosity of the melting eutectic formed from this ash, which contained 12.6 per cent of calcium oxide, a larger percentage of this basic oxide than was contained in any of the other samples.

## FUSIBILITY OF COAL ASH IN MIXTURES OF CARBON MONOXIDE AND CARBON DIOXIDE.

The investigations of Kreisinger, Ovitz, and Augustine<sup>a</sup> have shown that, with ordinary rates of combustion, oxygen is not found in appreciable quantities in a fuel bed at distances greater than 3 or 4 inches above the grate. Samples of gas taken at a point 3 inches above the grate contained approximately 12 per cent combustible gas (principally CO) and 14 per cent carbon dioxide. In view of this predominating proportion of CO and CO<sub>2</sub> it is even more important to know the effect of mixtures of these two gases on the fusibility of coal ash than to know the effect of hydrogen and water vapor.

### THEORETICAL CONSIDERATIONS.

Baur and Glaessner<sup>b</sup> found the following two series of equilibria in the system CO, CO<sub>2</sub>, Fe, FeO, and Fe<sub>3</sub>O<sub>4</sub>:



Their average values for the equilibrium constants are as follows:

*Equilibrium data of Baur and Glaessner.*

Reaction 1.		Reaction 2.	
Temperature of solid phase.	$\frac{p\text{CO}}{p\text{CO}_2}$	Temperature of solid phase.	$\frac{p\text{CO}}{p\text{CO}_2}$
° C.		° C.	
552	1.16	450	0.812
596	1.25	490	0.887
651	1.38	550	0.786
662	1.40	650	0.587
680	1.44	850	0.351
750	1.56	950	0.299
850	2.12		
900	2.51		

The equilibrium constants shown above are plotted in figure 19. Assuming that Fe<sub>2</sub>O<sub>3</sub> reacts like Fe<sub>3</sub>O<sub>4</sub> as regards reduction, it is evident that at temperatures up to 1,000° C. no reduction to metallic iron nor oxidation to Fe<sub>3</sub>O<sub>4</sub> can take place in a mixture of equal parts by volume of CO and CO<sub>2</sub>; and unless the direction of the two curves changes rather suddenly, FeO should continue to be the stable phase at higher temperatures, probably throughout the usual softening range of coal ashes. Although these conditions of equilibrium do not necessarily apply in the presence of other components as in a

<sup>a</sup> Kreisinger, Henry, Ovitz, F. K., and Augustine, C. E., Combustion in the fuel bed of hand-fired furnaces: Tech. Paper 137, Bureau of Mines, 1916, p. 39.

<sup>b</sup> Kreman, R. (translation by Potts, H. E.), The application of physico-chemical theory to technical processes and manufacturing methods: London, 1913, pp. 117-119.

coal-ash fusion, they at least point out the possibility of a minimum softening point due to ferrous iron in mixtures of approximately equal parts by volume of CO and CO<sub>2</sub>, provided this mixture is passed over the heated ash continuously, sweeping the gaseous products of the reaction out of the apparatus.

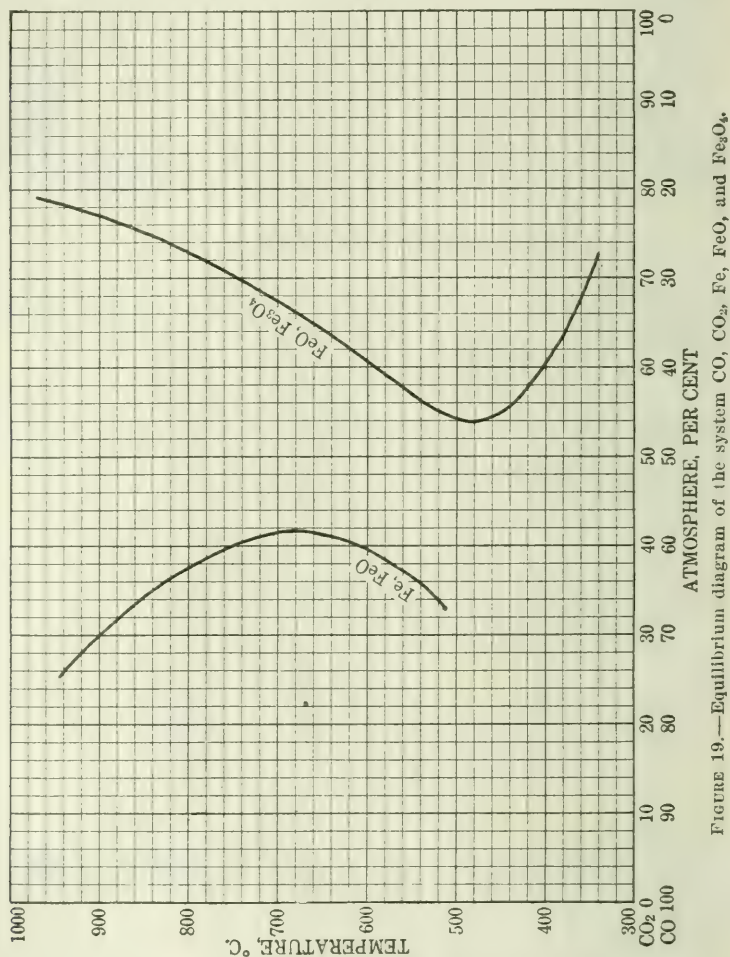


FIGURE 19.—Equilibrium diagram of the system CO, CO<sub>2</sub>, Fe, FeO, and Fe<sub>3</sub>O<sub>4</sub>.

#### METHOD OF CONDUCTING EXPERIMENTS.

Softening-temperature determinations were made in various mixtures of CO and CO<sub>2</sub> with ash from the same samples that were used in the series in which atmospheres of hydrogen and water vapor were used, except sample 15,845, which had been entirely used. The same type of furnace and of silica-tube arrangement was used, the hydrogen tank and saturator being replaced with a large gasometer which contained the desired mixture of CO and CO<sub>2</sub>. A gasometer



similar to one described by Dennis<sup>a</sup> was found especially advantageous for this work in that a large volume of gas could be made and stored without much change in composition taking place. Instead of the usual arrangement of having the gas confined over a considerable surface of liquid, the bell was arranged to move freely up and down between two concentric cylinders; the inner one was closed at the top, thus limiting the liquid seal to the 1-inch annular space between. By using a mixture of approximately 60 per cent glycerin and 40 per cent water the solubility of CO<sub>2</sub> was further reduced to a minimum.

#### PREPARATION OF GAS MIXTURES.

The mixtures containing equal parts of CO and CO<sub>2</sub> were made by heating 250 grams of oxalic acid and 600 c. c. of concentrated sulphuric acid in a 1,000-c.c. side-tube distilling flask. From the flask the gas passed through a wash bottle containing concentrated sulphuric acid and then directly into the gasometer, in which a slightly diminished pressure was maintained. Air in the gasometer and connections was first removed by partly filling and then emptying the tank before the gas was stored. Mixtures containing more than 50 per cent CO<sub>2</sub> were made by adding more CO<sub>2</sub> from a tank of liquid carbon dioxide. The carbon dioxide from this latter source showed the following analysis: Carbon dioxide, 99.9 per cent; air, 0.1 per cent.

Mixtures containing less than 50 per cent CO<sub>2</sub> were made by interposing between the oxalic acid generator and the gasometer an absorbing train of sodium hydroxide solution for removing CO<sub>2</sub>. CO<sub>2</sub> from the tank containing liquid CO<sub>2</sub> was then added to the CO in the gasometer. When the gasometer had been filled with the desired gas mixture the mixture was allowed to stand overnight to come to equilibrium. Samples were then taken over mercury and analyzed for carbon monoxide, carbon dioxide, and oxygen according to the Hempel method, as described in Technical Paper 63 of the Bureau of Mines.<sup>b</sup> Tests were made which assured the absence of any appreciable quantities of other combustible gases. In order to check any changes in the composition of the gas stored in the gasometer a sample was taken each day until the supply became exhausted. The change in composition from day to day never exceeded a few tenths of a per cent. Any small fractional percentage of oxygen found in the gas was calculated to CO<sub>2</sub>, on the assumption that in the furnace it combined with CO, an equivalent deduction being made in the CO percentage.

<sup>a</sup> Dennis, L. M., Gas analysis, 1913, pp. 25-27.

<sup>b</sup> Clement, J. K., Frazer, J. C. W., and Augustine, C. E., Factors governing the combustion of coal in boiler furnaces: Tech. Paper 63, Bureau of Mines, 1914, pp. 13-17, figs. 6 and 7.

## RESULTS OF EXPERIMENTS.

The general procedure followed in making the first series of softening-temperature tests in CO and CO<sub>2</sub> was identical with that used in the tests with hydrogen and water vapor, as described on pages 57 to 60. Heating with a temperature rise of 5° C. per minute until initial deformation, and then with a temperature rise of 2° C. per minute until the cone was down gave concordant results in the hydrogen atmosphere. The same rate of heating was therefore used in the first series in which carbon monoxide was used. However, as the work proceeded it soon became apparent that wholly concordant results were not being realized; as all previous investigations on the effect of rate of heating had been made in reference to atmospheres of air or of hydrogen and water vapor, it seemed possible that a slower rate of heating might be necessary to attain uniform results in CO-CO<sub>2</sub> atmospheres. The softening temperature of ash sample 13629 was therefore determined at three different rates of heating in a mixture of approximately equal parts of CO and CO<sub>2</sub>. As shown in the following table, when the rate of heat increase was 2° C. per minute, the ash softened at a temperature 72° C. lower than when the heat increase was 5° C. per minute.

*Results of experiments to determine effect of rate of heating on softening temperature of ash.*

Rate of temperature increase.	Softening temperature.	
	Initial.	Final.
5° C. per minute.....	° C. 1,072	° C. 1,176
5° C. to initial deformation, then 2° C. to final deformation.....	1,048	1,152
2° C. per minute.....	1,022	1,104

In view of this seemingly greater lag of the reducing and softening reactions in carbon monoxide a second series of tests was made on the same ashes at a much slower rate of heating. In this series the ash was heated rapidly to a temperature of 950° C. and held at that temperature for a period of one hour; heating was then continued at a 2° C. rate until the cone was down.

The results obtained in the two series are given in Table 10 following, and in the curves of figures 20 to 23; the previously obtained curves from experiments with mixtures of hydrogen and water vapor are also plotted to the same scale to permit comparison. The results of analyses of the ashes follow:

Results of analyses of ashes represented in figures 20 to 23 and in Table 10.

Ash sample No.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SO <sub>3</sub> .
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
16.....	37.2	25.5	11.8	1.5	12.6	1.9	1.4	0.3	5.6
5.....	42.2	30.6	19.0	1.2	1.3	1.0	1.3	2.9	.3
12.....	37.1	17.6	25.9	.7	3.2	.9	.4	1.8	2.3
9.....	54.8	27.0	7.0	1.3	4.3	1.7	.3	3.1	1.4

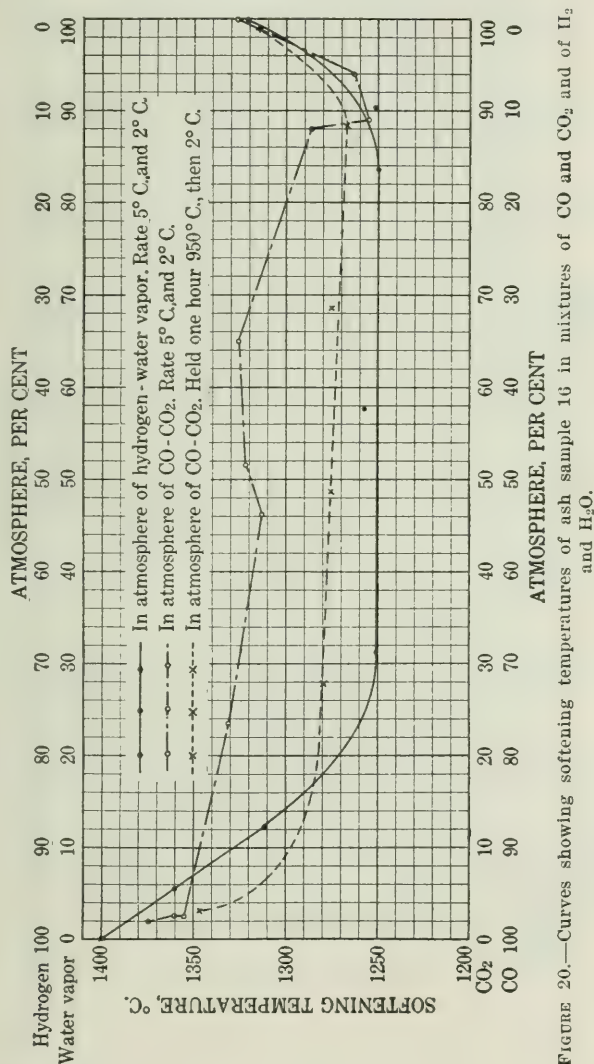


FIGURE 20.—Curves showing softening temperatures of ash sample 16 in mixtures of CO and CO<sub>2</sub> and of H<sub>2</sub> and H<sub>2</sub>O.



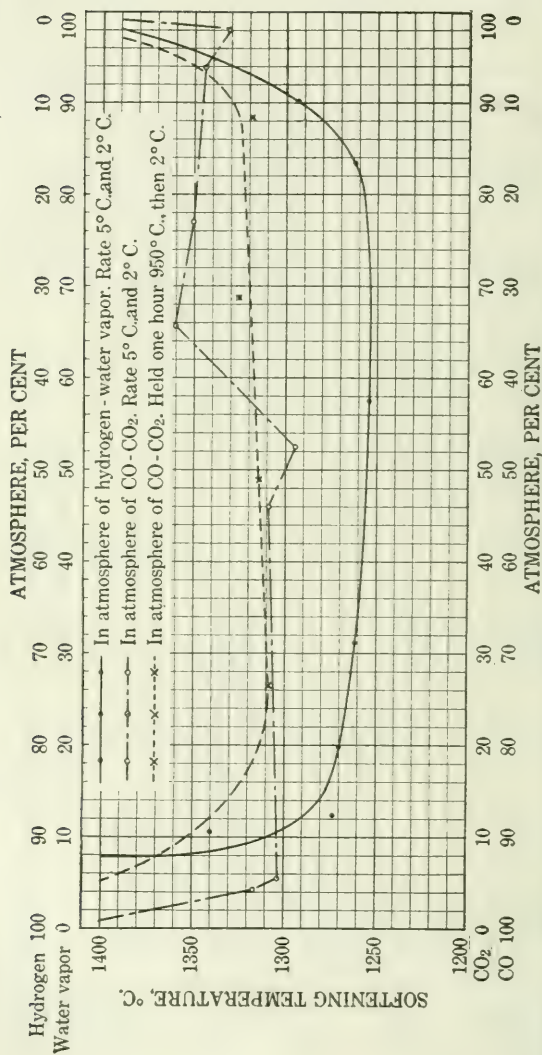


FIGURE 21.—Curves showing softening temperatures of ash sample 5 in mixtures of CO and CO<sub>2</sub> and of H<sub>2</sub> and H<sub>2</sub>O.

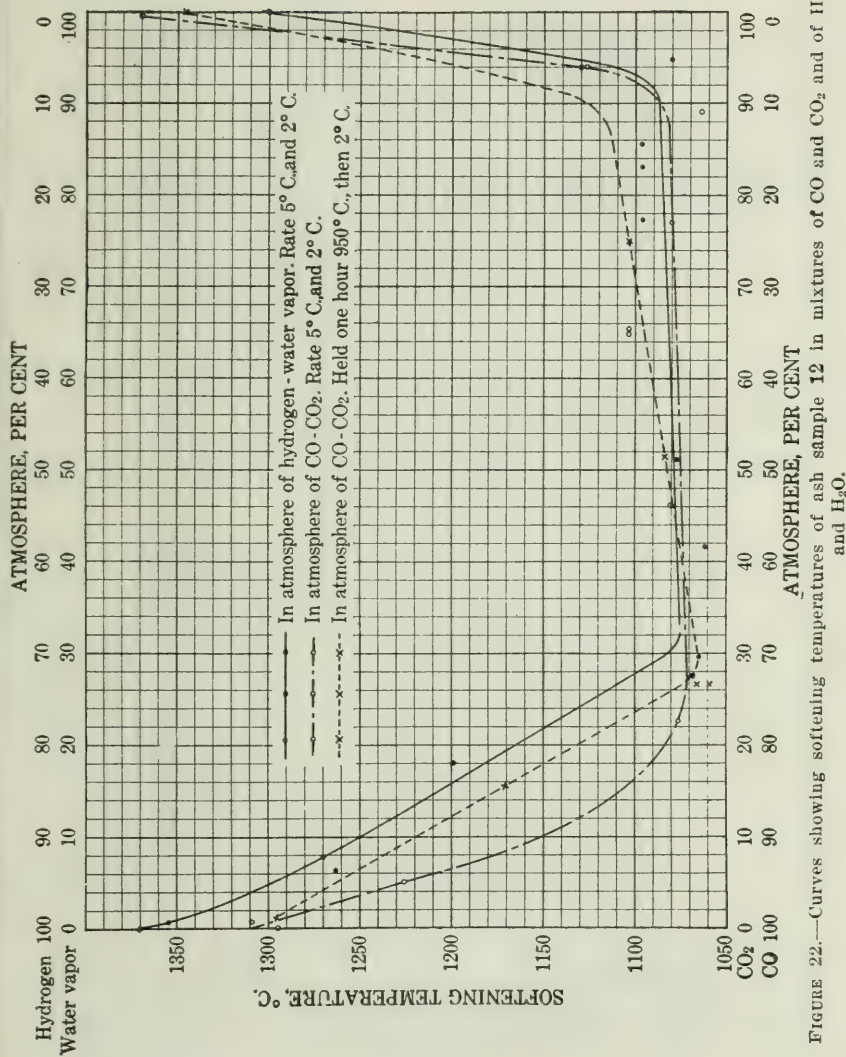


FIGURE 22.—Curves showing softening temperatures of ash sample 12 in mixtures of CO and CO<sub>2</sub> and of H<sub>2</sub> and H<sub>2</sub>O.

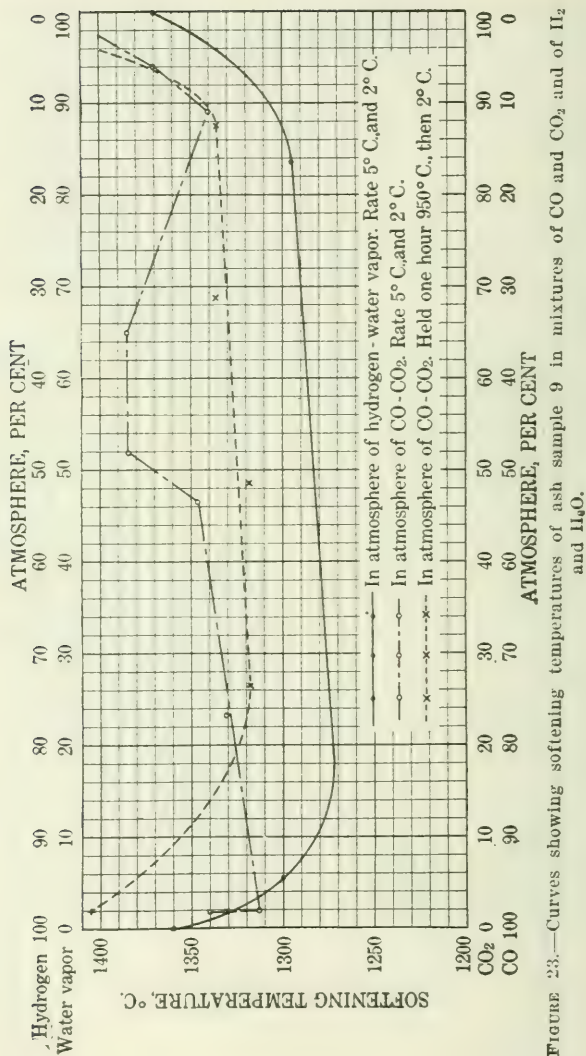


Figure 23.—Curves showing softening temperatures of ash sample 9 in mixtures of CO and CO<sub>2</sub> and of H<sub>2</sub> and H<sub>2</sub>O.



TABLE 10.—Results of tests to determine softening temperatures of certain ash samples in an atmosphere containing equal parts of CO and CO<sub>2</sub>.

## ASH SAMPLE 9.

Composition of gas.		Softening temperature at heating rate of 5° and 2° C. <sup>a</sup>	Softening temperature with temperature of 900° to 950° C. for 1 hour, followed by rise of 2° C. per minute.	Magnetic properties and amount of metallic iron in fused cone.
CO.	CO <sub>2</sub> .			
P. ct.	P. ct.	° C.	° C.	
98.2	1.8	{ 1,227-1,331	.....	Fairly magnetic; many small globules metallic Fe.
98.1	1.9	{ 1,276-1,340	.....	Faintly magnetic; many small globules metallic Fe.
98.0	2.0	{ 1,227-1,313	.....	Faintly magnetic; a few globules of metallic Fe.
76.7	23.3	1,227-1,331	1,271-1,405	Fairly magnetic; many small globules metallic Fe.
73.6	26.4	.....	1,136-1,318	Faintly magnetic; a few globules metallic Fe.
53.5	46.5	1,318-1,347	.....	Faintly magnetic; no metallic Fe.
51.7	48.3	.....	1,237-1,318	Do.
48.1	51.9	1,313-1,385	.....	Nonmagnetic; no metallic Fe.
35.2	64.8	1,350-1,385	.....	Do.
31.3	68.7	.....	1,175-1,337	Do.
12.7	87.3	.....	1,275-1,337	Do.
11.1	88.9	1,271-1,340	.....	Do.
6.0	94.0	1,304-1,370	.....	Do.
.9	99.1	.....	Above 1,400	Faintly magnetic; no metallic Fe.
.3	99.7	<sup>b</sup> Above 1,400	.....	Fairly magnetic; no metallic Fe.

<sup>a</sup> A cone heated for 2 hours at 900° to 950° C. and then subjected to a temperature rise of 2° C. per minute thereafter started to bend at 1,174° C. and was down at 1,314° C.

<sup>b</sup> Just started.

## ASH SAMPLE 16.

98.1	1.9	1,327-1,375	.....	Strongly magnetic; many globules metallic Fe.
97.5	2.5	{ 1,313-1,355	.....	Fairly magnetic; many globules metallic Fe.
97.0	3.0	{ 1,322-1,360	.....	Do.
76.7	23.3	1,252-1,331	1,318-1,347	Strongly magnetic; many globules metallic Fe.
72.3	27.7	.....	1,167-1,279	Fairly magnetic; many globules metallic Fe.
53.9	46.1	1,275-1,313	.....	Fairly magnetic; a few globules metallic Fe.
51.7	48.3	.....	1,149-1,275	Faintly magnetic; very few globules metallic Fe.
48.4	51.6	1,300-1,322	.....	Faintly magnetic; no metallic Fe.
35.2	64.8	1,300-1,326	.....	Do.
31.5	68.5	.....	1,133-1,275	Do.
12.0	88.0	1,174-1,287	.....	Lost.
11.7	88.3	.....	1,237-1,267	Nonmagnetic; no metallic Fe.
11.1	88.9	1,248-1,255	.....	Do.
6.0	94.0	1,227-1,263	.....	Fairly magnetic; no metallic Fe.
.9	99.1	.....	1,233-1,314	Strongly magnetic; no metallic Fe.
.0	100.0	1,275-1,327	.....	Do.

<sup>c</sup> A cone heated 2 hours at 900° to 950° C. and then subjected to a temperature rise of 2° C. per minute thereafter started to bend at 1,184° C. and was down at 1,275° C.

## ASH SAMPLE 5.

98.2	1.8	.....	1,251-d1,400	Fairly magnetic; many globules metallic Fe.
98.1	1.9	( <sup>c</sup> )	.....	Strongly magnetic; many globules metallic Fe.
95.8	4.2	1,199-1,317	.....	Do.
94.8	5.2	1,176-1,304	.....	Fairly magnetic; many globules metallic Fe.
73.6	26.4	.....	1,220-1,309	Faintly magnetic; no metallic Fe.
64.0	46.0	1,300-1,309	.....	Nonmagnetic; no metallic Fe.
51.1	48.9	.....	1,080-1,314	Do.
47.5	52.5	1,248-1,295	.....	Do.
35.2	64.8	1,160-1,360	.....	Faintly magnetic; no metallic Fe.
31.3	68.7	.....	1,267-1,327	Do.
23.1	76.9	1,322-1,350	.....	Nonmagnetic; no metallic Fe.
11.7	88.3	.....	1,122-1,318	Fairly magnetic; no metallic Fe.
6.1	93.9	1,127-1,345	.....	Faintly magnetic; no metallic Fe.
2.1	97.9	1,142-1,331	.....	Lost.
.9	99.1	.....	Above 1,400	Strongly magnetic; no metallic Fe.
.0	100.0	Above 1,400	.....	Do.

<sup>d</sup> Above.

<sup>c</sup> Cone started softening at 1,243° C.; one-half melted down at 1,400° C.

TABLE 10.—*Results of tests to determine softening temperatures of certain ash samples in an atmosphere containing equal parts of CO and CO<sub>2</sub>—Continued.*

## ASH SAMPLE 12.

Composition of gas.		Softening temperature at heating rate of 5° and 2° C. <sup>a</sup>	Softening temperature with temperature of 900° to 950° C. for 1 hour, followed by rise of 2° C. per minute.	Magnetic properties and amount of metallic iron in fused cone.
CO.	CO <sub>2</sub> .			
<i>P. ct.</i>	<i>P. ct.</i>	° C.	° C.	
100.0	0.0	1,270-1,295	.....	Strongly magnetic; much metallic Fe.
99.2	.8	1,241-1,309	.....	Do.
99.0	1.0	.....	1,251-1,296	Strongly magnetic; many globules metallic Fe.
95.0	5.0	1,170-1,226	.....	Strongly magnetic; much metallic Fe.
84.7	15.3	.....	1,101-1,171	Fairly magnetic; many globules metallic Fe.
77.3	22.7	<i>f</i> 1,076	.....	Faintly magnetic; no metallic Fe.
73.4	26.6	.....	<i>a</i> 1,058	Nonmagnetic; No metallic Fe.
73.4	26.6	.....	1,055-1,066	Do.
53.9	46.1	1,050-1,080	.....	Nonmagnetic; no metallic Fe.
48.5	51.5	.....	1,073-1,083	Do.
47.7	52.3	1,027-1,048	.....	Faintly magnetic; no metallic Fe.
35.2	64.8	1,072-1,104	.....	Nonmagnetic; no metallic Fe.
25.1	74.9	.....	1,073-1,104	Do.
23.1	76.9	<i>f</i> 1,104	.....	Lost.
		<i>f</i> 1,080	.....	Nonmagnetic; no metallic Fe.
11.1	88.9	1,048-1,064	.....	Fairly magnetic; no metallic Fe.
		1,060-1,130	.....	Do.
6.0	94.0	1,048-1,127	.....	Do.
.3	99.7	1,304-1,370	.....	Strongly magnetic; no metallic Fe.
.0	100.0	.....	1,300-1,347	Do.

<sup>a</sup> Starting point not observed.

## DISCUSSION OF RESULTS.

The softening-point curves show that, except ash sample 16243, smooth curves were not obtained for the softening points in atmospheres of CO and CO<sub>2</sub> when the rate of increase of heating was 5° and 2° C. per minute; however, on allowing more time for reduction and softening of the ash by holding the cone at a temperature of 900° to 950° for a period of one hour and then increasing the heat 2° C. per minute until softening was complete, the seeming irregularities disappeared and curves similar in shape to those obtained in atmospheres of hydrogen and water vapor were obtained. These lower and more uniform curves show for each of the ashes tested a well-defined region of minimum softening temperature, which ranged between approximate limits of 75 and 10 per cent carbon monoxide. For most samples the minimum softening temperature in an atmosphere of carbon monoxide and carbon dioxide was somewhat higher than the softening temperature in an atmosphere of hydrogen and water vapor, the greatest difference being 65° C. for sample 15844.

The general similarity in shape of the H<sub>2</sub>-H<sub>2</sub>O and the CO-CO<sub>2</sub> curves would indicate that the variation in the fusibility of a given ash is determined principally by the state of oxidation of its iron content. The stable phase of iron is in turn determined by the temperature, by the relative concentrations of oxidizing and reducing

gases, and, in part, by the other components of the ash. In a general way the effect as regards reduction would be similar for carbon monoxide and hydrogen; likewise the oxidizing effects of air, of carbon dioxide, and of water vapor on the iron component are similar enough to give maximum softening temperatures of the same order for a given ash, as shown in Table 11 following:

TABLE 11.—*Results of tests to determine comparative effects on softening temperatures of ash of atmospheres of air, of water vapor, of carbon dioxide, of carbon monoxide, of equal parts of hydrogen and water vapor, and of equal parts of carbon monoxide and carbon dioxide.*

Ash sample No.	Per cent of Fe <sub>2</sub> O <sub>3</sub> .	Softening temperature, ° C.						
		Oxidizing atmosphere.			Reducing atmosphere.		Atmosphere of equal parts of H <sub>2</sub> and H <sub>2</sub> O.	Atmosphere of equal parts of CO and CO <sub>2</sub> .
		Air.	Water vapor.	CO <sub>2</sub> .	H <sub>2</sub> .	CO.		
16243.....	35.9	1,335	1,313	1,347	1,370	1,295	1,080	1,085
15844.....	19.0	1,490	(a)	(a)	(a)	(a)	1,255	1,315
16586.....	11.8	1,322	1,322	1,327	1,402	1,375	1,250	1,275
15848.....	7.0	1,425	1,370	(a)	1,360	1,331	1,283	1,325

a Above 1,400.

The sharp rise of the softening-point curves at both the oxidizing and reducing end confirms the reasons previously advanced for the large variations in results obtained in different furnaces. It is evident that no concordant results can be obtained in oxidizing atmospheres containing small proportions of reducing gas or similarly in essentially reducing atmospheres with small admixtures of oxidizing gases, as in these regions the curves have a sharp inclination.

#### RELATION OF SOFTENING TEMPERATURES IN ATMOSPHERES OF HYDROGEN AND WATER VAPOR, AND OF CARBON MONOXIDE AND CARBON DIOXIDE TO CLINKER FORMATION IN FURNACES.

The general form of the softening-point curves suggests a choice of three types of atmosphere in which uniform softening points may be determined, namely, (1) a strongly reducing atmosphere of 100 per cent hydrogen or carbon monoxide; (2) a weakly reducing atmosphere of approximately 50 per cent hydrogen and 50 per cent water vapor, or of 50 per cent carbon monoxide and 50 per cent carbon dioxide; (3) an oxidizing atmosphere of 100 per cent water vapor, carbon dioxide, or air.

The atmosphere to be selected for a standard softening-temperature test should be one that produces a slag with the iron in the same state of oxidation as is usually found in fuel-bed clinkers. Determinations were therefore made of the relative percentages of ferrous, ferric, and metallic iron in the glassy parts of furnace clinkers and in the ash cones fused in the atmospheres mentioned above.



**FERROUS, FERRIC, AND METALLIC IRON IN FUSED ASH CONES AND CLINKER SLAGS.**

Fourteen to twenty ash cones, whose weight aggregated 2 or 3 grams, were placed in a platinum boat and heated to softening temperatures in the silica tube of the furnace at the different rates of heating used in the previous tests. In the tests with an atmosphere of hydrogen and water vapor the boat and its contents were held at this temperature for 30 minutes to permit the softening reactions to approach equilibrium. In the tests with an atmosphere of CO and CO<sub>2</sub> heating was stopped as soon as the softening point was reached. As in the softening-temperature determinations the cones were heated to redness previous to the tests to oxidize and remove the organic binders. At the end of the heating period the electric current was cut off and the furnace allowed to cool rapidly, without interrupting the gas stream. To avoid any possibility of change during cooling it would have been better to have quenched the fusion suddenly. However, the viscosity of the ash melted was so great that little change was probable at the rate of cooling used. The fused material appeared glassy.

As the particular ash samples used in the softening-temperature tests and in the fusions with hydrogen and water vapor became exhausted before the fusions in atmospheres of CO and CO<sub>2</sub> were made, it was necessary to use for the latter fusion tests other samples of ash from coal from the same mines. The new samples showed a slightly different total iron content and a softening temperature that deviated approximately 40° C. from that of the original samples. However, they served as well for use in determining the relative reducing effect of the different atmospheres on the ferric oxide.

After the furnace had cooled, the fused cones were removed from the boat and were pulverized, first by impact in a diamond mortar of hardened steel and then in an agate mortar, to 100 mesh and analyzed for ferrous, ferric, and metallic iron by the method of Mathesius.<sup>a</sup> The results, as given in Table 12 following, show well-defined differences in the state of oxidation of the iron content of the fused ash samples in the various atmospheres. In air, water vapor, and carbon dioxide 67 to 88 per cent of the ferric oxide remained as ferric iron; in hydrogen and in carbon monoxide, 49 to 78 per cent of the iron was reduced to the metallic form, the larger percentage being found in the cones fused in hydrogen atmosphere; in the cones fused in an atmosphere of equal parts of hydrogen and water and in the cones fused in an atmosphere of equal parts of CO and CO<sub>2</sub> little or no metallic iron was found, the dominant form being ferrous iron, the proportion of which ranged from 78 to 94 per cent.

<sup>a</sup> Mathesius, Ludwig, Untersuchungen über die Reduzierbarkeit von Eisenerzen in strömenden Gasen: Stahl und Eisen, Bd. 34, 1914, pp. 866-867.

TABLE 12.—Results of analyses of ash cones fused in various atmospheres and of furnace clinkers.

## GROUP I. FERRIC IRON PREDOMINATING.

Sample No.	Description of sample.	Atmosphere.	Rate of temperature rise per minute.	Maximum temperature of fusion, ° C.	Total Fe.	Percentage of total Fe occurring as—			Character of slag.
						Metallic iron.	Ferrous iron.	Ferric iron.	
20155.	Ash.....	CO <sub>2</sub> .....	5° and 2° C.a.	1,405	P. ct. 6.7	None.	12	88	Glassy, black; slightly magnetic.
20155.	.....do.....	.....do.....	(b)	1,405	6.8	None.	24	76	Glassy, black; nonmagnetic.
20242.	.....do.....	.....do.....	5° and 2° C.a.	1,368	21.4	None.	28	72	Black, glassy; highly magnetic.
20242.	.....do.....	.....do.....	(b)	1,368	21.3	None.	33	67	Do.
16243.	.....do.....	H <sub>2</sub> O vapor.	5° and 2° C.a.	1,300	27.9	Trace.	28	72	Glassy, black, highly magnetic.
13629.	.....do.....	Air.....	.....do.....	1,400	15.5	Trace.	30	70	Dark red to almost black, glassy; highly magnetic.

## GROUP II. METALLIC IRON PREDOMINATING.

20155.	Ash.....	96 CO; 4 CO <sub>2</sub>	5° and 2° C.a.	1,337	6.6	49	41	10	Dark gray; magnetic.
20155.	.....do.....	.....do.....	(b)	1,405	6.2	55	32	13	Do.
20242.	.....do.....	99 CO; 1 CO <sub>2</sub>	5° and 2° C.a.	1,309	20.7	60	36	4	Dark gray; highly magnetic.
20242.	.....do.....	97 CO; 3 CO <sub>2</sub>	(b)	1,309	21.9	62	38	Trace	Do.
16243.	.....do.....	H <sub>2</sub> .....	5° and 2° C.a.	1,370	28.6	78	21	1	Black; metallic luster.

## GROUP III. FERROUS IRON PREDOMINATING.

20155.	Ash.....	48 CO; 52 CO <sub>2</sub>	5° and 2° C.a.	1,368	6.6	None.	81	19	Dark gray; slightly magnetic.
20155.	.....do.....	.....do.....	(b)	1,405	5.7	None.	78	22	Do.
20242.	.....do.....	47 CO; 53 CO <sub>2</sub>	5° and 2° C.a.	1,080	20.9	4	88	8	Dark, glassy; slightly magnetic.
20242.	.....do.....	.....do.....	(b)	1,080	20.9	6	79	15	Do.
20242.	.....do.....	48 CO; 52 CO <sub>2</sub>	5° and 2° C.a.	1,368	20.4	7	87	6	Do.
20242.	.....do.....	.....do.....	(b)	1,370	19.8	8	84	8	Do.
16243.	.....do.....	50 H <sub>2</sub> ; 50 H <sub>2</sub> O.	5° and 2° C.a.	1,080	27.4	Trace.	82	18	Black, glassy; nonmagnetic.
15848.	.....do.....	.....do.....	.....do.....	1,280	4.7	6	94	Trace	Gray, glassy; nonmagnetic.
20137.	Clinker from a hand-fired furnace.	.....do.....	.....do.....	.....do.....	14.5	12	79	9	Dark, glassy; contained some magnetic pieces.
20145.	Clinker from boiler furnace.	.....do.....	.....do.....	.....do.....	12.7	6	75	19	Brown and black, glassy; contained some magnetic pieces.
20452.	.....do.....	.....do.....	.....do.....	.....do.....	8.9	9	75	16	Do.

a Cone heated with a temperature rise of 5° C. per minute until initial deformation when the rate of increase was 2° C. per minute until final deformation.

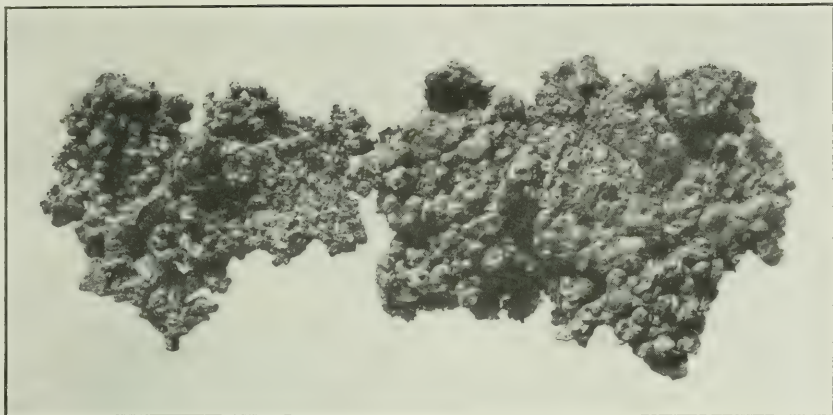
b Cone heated for 1 hour at 950° C., when it was subjected to a temperature rise of 2° C. per hour.

Together with the results of analyses of fused ash cones are given the results of analyses of the fused and glassy parts of several clinkers produced under working conditions in the fuel beds of different boiler furnaces operating with Pittsburgh coal. The coal, however, came from different mines. Clinker 20137 was obtained from the grate of a small hand-fired experimental furnace used for combustion investigations. Clinkers 20145 and 20452 were kindly furnished by Mr. A. A. Straub, steam engineer of the Duquesne Light Co., of Pittsburgh, Pa. These clinkers were dumped from the fuel bed while hot and were quenched with water. The clinkers were of the particularly troublesome taffylike variety that flow over the grate bars and shut off the air supply for combustion. Plate III, A, represents a photograph of clinker 20452. The edge at the top of the plate is the side that adhered to the corrugated grate of the new model type D Roney stoker. The matrix of this clinker was a black glass which could readily be chipped out in quantity for analysis without including any coke or unfused material. At the contact surface of coke and slag, particles of metallic iron could be identified. A microscopic examination, made by Mr. A. A. Klein, of the Bureau of Standards, of the powdered slag from this clinker and from the others showed the material to be essentially a glass with small quantities of sillimanite ( $\text{Al}_2\text{O}_3, \text{SiO}_2$ ) and of an opaque iron mineral, probably magnetite, as the only crystalline phases present.

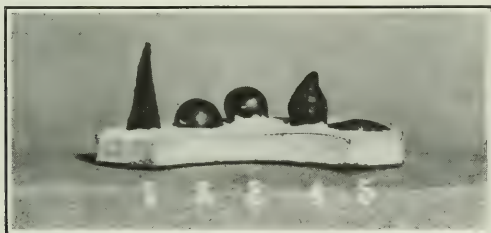
The results of analyses of the fused ash cones, and of the three fuel-bed clinkers given in Table 12 show that of the different atmospheres employed in the laboratory furnace, the atmosphere containing equal parts of hydrogen and water vapor and that containing equal parts of carbon monoxide and carbon dioxide produced slags that corresponded most closely in the state of oxidation of their iron content to the glassy parts of the furnace clinkers. In both the fused cones and the clinkers approximately 80 per cent of the iron appeared as ferrous iron, the form in which it imparts the maximum fluxing action on the silicate mixture.

In view of the results presented above, the conclusion is warranted that the minimum softening temperature of a coal ash as determined in either the  $\text{CO-CO}_2$  or the  $\text{H}_2\text{-H}_2\text{O}$  atmosphere is more representative of the temperature of clinker formation under furnace conditions than the somewhat higher results obtained in strongly reducing atmospheres of hydrogen or carbon monoxide, on the one hand, and oxidizing atmospheres of air, water vapor, or carbon dioxide, on the other.





A. CLINKER NO. 20452 FROM GRATE OF RONEY STOKER.



B. TYPICAL FORMS OF CONES FUSED IN THE NO. 3 MELTER'S FURNACE.



**RELATIVE MERITS OF CO-CO<sub>2</sub> AND OF H<sub>2</sub>-H<sub>2</sub>O ATMOSPHERES AS STANDARD ATMOSPHERES FOR FUSION TESTS.**

The results of the experiments with the four ashes that have been investigated indicate that the effects of hydrogen and of carbon monoxide as a reducing agent are closely similar. The principal effect of either gas mixture is to cause the iron component to appear in the slag in the ferrous state. There are, however, certain minor reactions involving the formation of sulphides and carbides that proceed differently in the two atmospheres. For example, all the ash cones fused in an atmosphere containing equal parts of CO and CO<sub>2</sub> and in an atmosphere of 100 per cent CO, contained ferrous sulphide and some of the fused cones contained carbides; the sulphides were formed by reduction of sulphates in the ash. In the fusions made in an H<sub>2</sub>-H<sub>2</sub>O atmosphere special evidence of sulphide formations was not noted. Obviously carbides could not be formed in the latter atmosphere. These minor reactions and perhaps a slower reaction velocity of reduction may be the cause of the somewhat higher softening temperatures obtained in the CO-CO<sub>2</sub> mixtures.

In order to obtain further data on the relation between the minimum softening temperatures of various ashes, as determined in an atmosphere containing equal parts of H<sub>2</sub> and H<sub>2</sub>O, in an atmosphere containing equal parts of CO and CO<sub>2</sub>, and in air, many samples of coal ashes having various contents of iron oxide were tested in these atmospheres.

The results are given in Table 13, following, and are plotted in the order of increasing iron oxide content in figures 24 and 25. Table 13 and figure 24 also present a series of results obtained in gas furnace No. 3. These values are discussed in a subsequent part of this report.



**TABLE 13.**—*Results of tests to determine softening temperatures of coal ashes containing various percentages of ferric oxide in various atmospheres.*  
 [Each cone  $\frac{1}{8}$  inch, mounted in a vertical position in quartz tube in furnace shown in figure 17, except certain tests in a gas furnace; rate of increase of heating for tests in atmosphere of equal parts of  $H_2$  and  $H_2O$ ,  $5^\circ C.$  per minute until initial deformation, then  $2^\circ C.$  per minute; for tests in atmosphere of equal parts of  $CO$  and  $CO_2$ , rate of increase of heating was  $2^\circ C.$  per minute.]

Ash sample No.	$Fe_2O_3$ in ash.	Softening temperature in atmosphere of:				Differences.				Softening interval.				Magnetism of cones fused in atmosphere of equal parts of $CO$ and $CO_2$ .
		Equal parts of $H_2$ and $H_2O$ .	Equal parts of $CO$ and $CO_2$ .	Gas furnace.	Air.	Atmosphere of $H_2$ and $H_2O$ and atmosphere of $CO$ and $CO_2$ .	Atmosphere of $H_2$ and $H_2O$ and atmosphere of $CO$ and $CO_2$ .	Atmosphere of $CO$ and $CO_2$ .	Atmosphere of gas and furnace and atmosphere of $CO$ and $CO_2$ .	$H_2-H_2O$ atmosphere.	$CO-CO_2$ atmosphere.	Atmosphere of gas furnace.	Air.	
96	P. $\alpha$ . 5.0	$^\circ C.$ 1,263	$^\circ C.$ 1,254	$^\circ C.$ 1,286	$^\circ C.$ 1,278	$^\circ C.$ 15	$^\circ C.$ 60	$^\circ C.$ 24	$^\circ C.$ 12	$^\circ C.$ 36	$^\circ C.$ 4	$^\circ C.$ 5	$^\circ C.$ 5	Not magnetic.
92	5.9	1,345	1,361	1,361	1,463	118	90	58	— 44	125	134	21	44	Do.
97	6.5	1,313	1,292	1,236	1,345	32	21	53	— 56	42	70	36	36	Slightly magnetic.
75	6.8	1,327	1,405	1,469	1,520	193	78	115	— 64	36	122	38	64	Not magnetic.
9	7.0	1,271	1,360	1,369	1,425	59	330	95	— 39	92	177	54	55	Do.
77	7.0	1,300	1,360	1,401	1,470	60	170	110	— 41	77	89	113	60	Do.
93	7.4	1,227	1,288	1,325	1,370	61	143	82	— 37	54	107	148	20	Do.
96	7.8	1,209	1,345	1,262	1,500	136	345	155	— 83	51	181	158	60	Do.
85	8.0	1,228	1,233	1,240	1,320	92	150	87	— 7	37	83	84	20	Do.
73	8.2	1,255	1,405	1,358	1,450	195	150	45	— 47	49	214	176	120	Do.
76	8.4	1,205	1,261	1,250	1,400	195	56	139	— 11	56	91	21	120	Do.
71	9.0	1,179	1,320	1,298	1,465	286	141	145	— 22	75	193	90	65	Do.
18	9.0	1,187	1,305	1,277	1,400	213	148	65	— 58	52	186	121	60	Do.
74	9.2	1,227	1,370	1,327	1,405	178	143	35	— 43	35	230	122	75	Do.
75	9.4	1,216	1,293	1,310	1,407	191	169	82	— 15	31	134	138	67	Do.
78	9.5	1,212	1,271	1,282	1,370	183	139	134	— 31	38	149	48	55	Do.
69	9.5	1,161	1,197	1,166	1,405	189	59	153	— 11	6	85	36	98	Do.
72	9.8	1,173	1,370	1,304	1,426	253	197	56	— 66	69	243	75	96	Do.
17	10.1	1,198	1,201	1,218	1,343	145	3	142	— 17	41	27	62	63	Do.
64	10.3	1,251	1,310	1,240	1,474	183	169	164	— 70	100	120	32	65	Do.
68	10.5	1,173	1,350	1,229	1,550	28	28	177	— 28	25	51	73	97	Do.
99	11.3	1,201	1,215	1,197	1,269	98	14	84	— 18	10	93	41	10	Do.
16	11.8	1,251	1,261	1,261	1,322	71	61	61	— 0	24	49	53	82	Do.
82	11.9	1,181	1,310	1,325	1,456	275	129	146	— 15	63	177	64	66	Do.
79	12.4	1,149	1,310	1,336	1,414	265	161	104	— 26	48	170	21	46	Do.
89	13.1	1,155	1,292	1,325	1,369	214	137	77	— 33	75	222	143	12	Do.
65	13.6	1,165	1,190	1,166	1,409	244	244	219	— 24	24	50	36	27	Do.
81	14.3	1,143	1,202	1,166	1,369	275	128	147	— 35	42	131	96	38	Do.
90	15.0	1,170	1,212	1,304	1,418	154	128	112	— 16	16	42	47	31	Do.
70	16.6	1,148	1,335	1,176	1,410	262	187	75	— 159	44	182	31	28	Do.

8.....	18.0	1,205	1,365	1,320	1,450	160	245	85	+ 45	41	273	5	10	Slightly magnetic.
80.....	18.1	1,167	1,360	1,226	1,430	153	263	110	+ 94	66	170	32	30	Do.
67.....	18.3	a <sub>1</sub> , 185	1,360	1,316	1,430	175	263	190	+ 44	50	258	69	10	Not magnetic.
100.....	18.9	b <sub>1</sub> , 196	1,212	1,172	1,377	16	181	165	+ 40	31	142	26	20	Do.
5.....	19.0	1,255	1,314	1,340	1,490	59	235	176	+ 26	82	181	54	50	Do.
66.....	19.5	a <sub>1</sub> , 188	1,212	1,218	1,340	24	152	128	- 6	23	22	62	10	Do.
83.....	20.0	a <sub>1</sub> , 116	1,190	1,145	1,368	74	252	178	+ 45	36	140	41	31	Slightly magnetic.
11.....	20.4	a <sub>1</sub> , 132	1,143	1,156	1,400	11	268	257	- 13	47	62	26	20	Not magnetic.
10.....	22.4	a <sub>1</sub> , 137	1,153	1,187	1,310	16	173	157	- 34	10	45	42	40	Do.
98.....	23.5	1,105	1,104	1,166	1,322	- 1	217	218	- 62	55	82	87	13	Do.
93.....	24.9	1,127	1,170	1,198	1,370	- 43	243	200	- 28	23	78	84	20	Do.
84.....	26.8	1,108	1,092	1,120	1,276	- 16	168	184	- 28	28	7	84	26	Do.
94.....	29.7	1,185	1,268	1,272	1,345	- 83	160	77	- 4	4	87	64	70	Slightly magnetic.
97.....	31.5	a <sub>1</sub> , 119	1,092	1,116	1,365	27	186	213	- 24	33	28	12	26	Not magnetic.
91.....	34.6	1,263	1,292	1,341	1,497	29	234	205	- 49	90	133	211	97	Slightly magnetic.
12.....	35.9	a <sub>1</sub> , 060	1,080	1,064	1,335	20	275	255	+ 16	12	30	10	65	Do.
86.....	41.9	1,071	1,077	1,076	1,358	6	287	281	+ 1	6	51	27	37	Not magnetic.
88.....	61.7	a <sub>1</sub> , 113	1,130	1,125	1,452	17	339	322	+ 5	0	18	15	152	Slightly magnetic.
Average...	15.9	1,193	1,259	1,249	1,393	66	200	134	10	44	117	63	49	

<sup>a</sup> Cone  $\frac{1}{16}$  by 1 inch, mounted vertically in molybdenum furnace shown in figure 29.

<sup>b</sup> Atmosphere of 60 per cent H<sub>2</sub> and 40 per cent H<sub>2</sub>O used instead of 50 per cent of each.

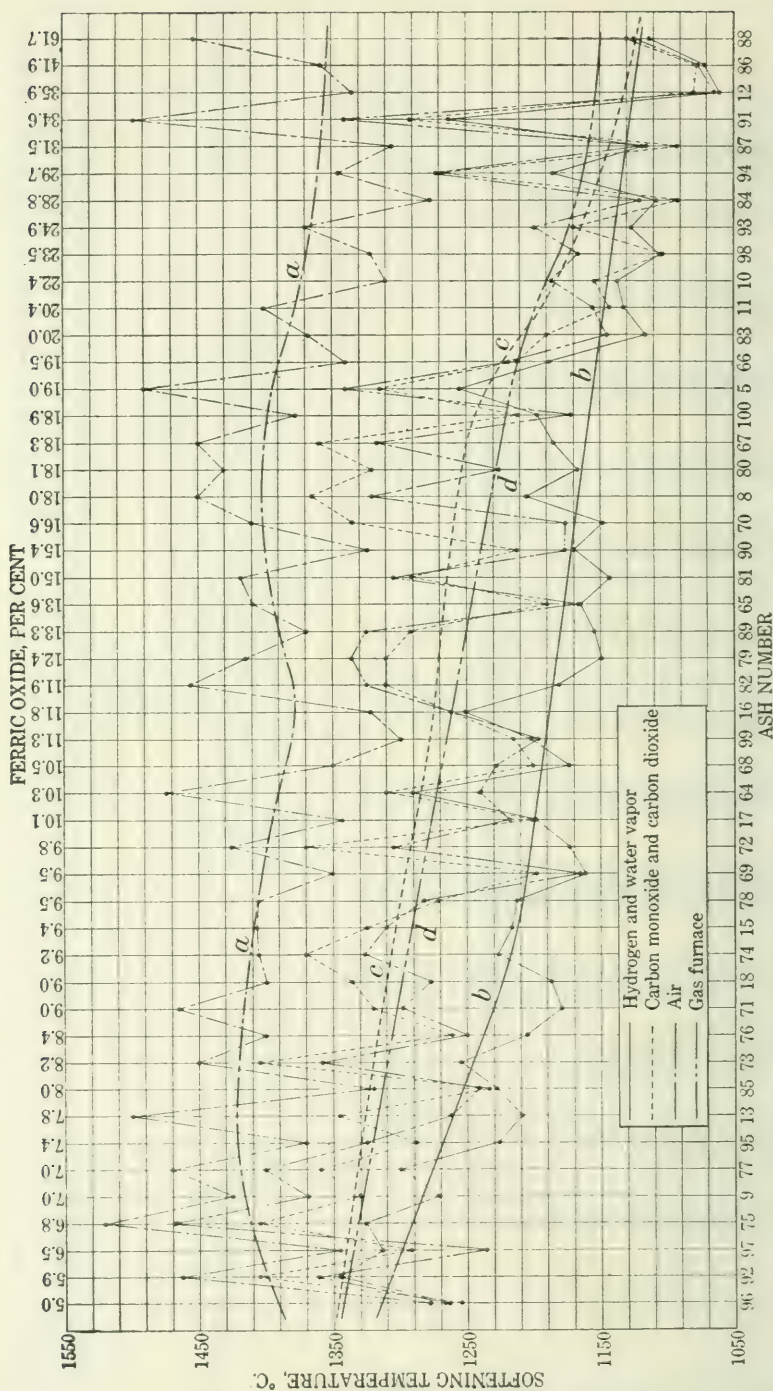


FIGURE 24.—Curves showing softening temperatures of coal ash in atmospheres of equal parts of  $H_2$  and  $H_2O$ , equal parts of  $CO$  and  $CO_2$ , gas furnace No. 3, and air, with especial reference to the percentage of  $Fe_2O_3$  in the ash. *a*, Average curve showing relation between softening temperature in air and percentage of  $Fe_2O_3$  in ash; *b*, average curve showing relation between softening temperature in atmosphere of equal parts of  $H_2$  and  $H_2O$  and percentage of  $Fe_2O_3$  in ash; *c*, average curve showing relation between softening temperature in atmosphere of equal parts of  $CO$  and  $CO_2$  and percentage of  $Fe_2O_3$  in ash; *d*, average curve showing relation between softening temperature in gas furnace No. 3 and percentage of  $Fe_2O_3$  in ash.

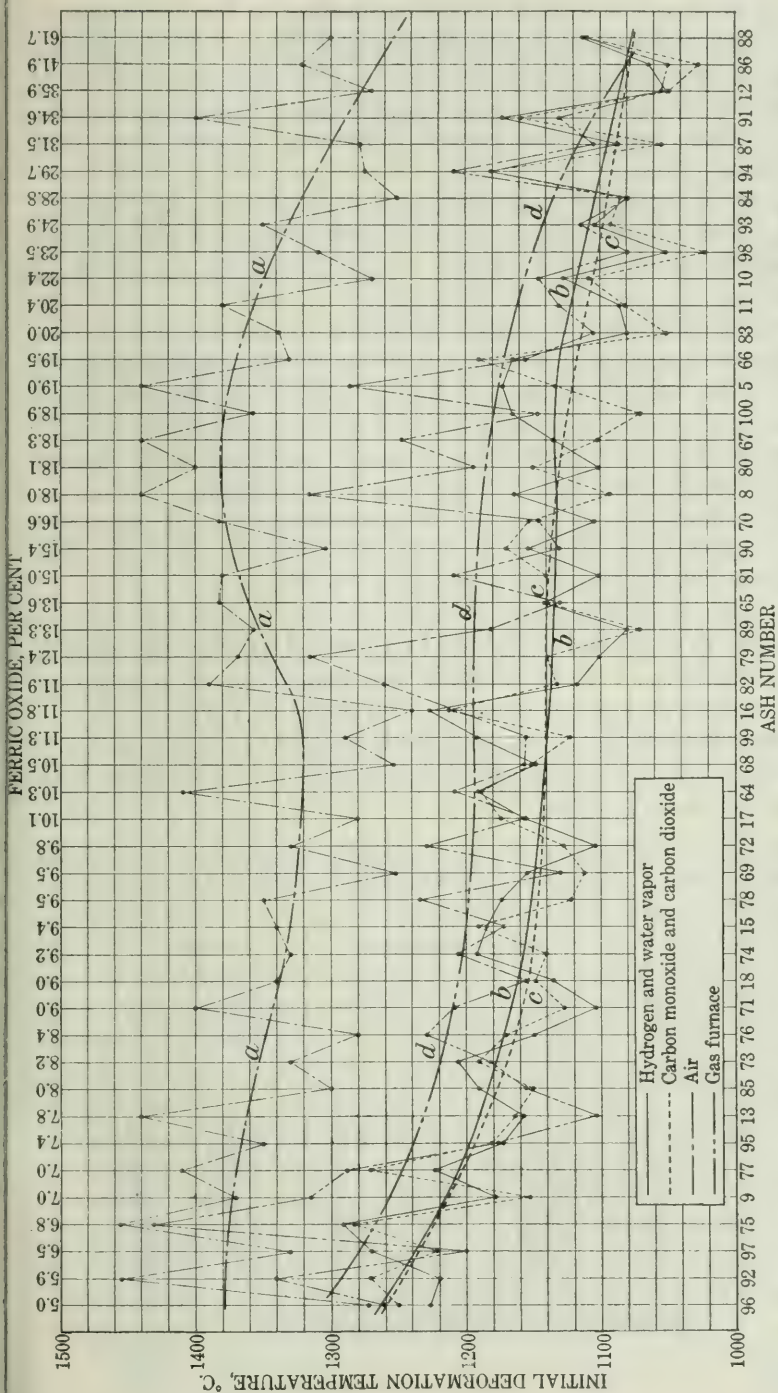


FIGURE 25.—Curves showing initial deformation points of coal ash in atmospheres of equal parts of  $H_2$  and  $H_2O$ , equal parts of  $CO$  and  $CO_2$ , gas furnace No. 3, and air, with special reference to the percentage of  $Fe_2O_3$  in the ash. *a*, Average curve showing relation between initial deformation point in air and percentage of  $Fe_2O_3$  in ash; *b*, average curve showing relation between initial deformation point in atmosphere of equal parts of  $H_2$  and  $H_2O$  and percentage of  $Fe_2O_3$  in ash; *c*, average curve showing relation between initial deformation point in atmosphere of equal parts of  $CO$  and  $CO_2$  and percentage of  $Fe_2O_3$  in ash; *d*, average curve showing relation between initial deformation point in gas furnace No. 3 and percentage of  $Fe_2O_3$  in ash.



It will be seen from figure 25 that softening of the ash began in reducing atmospheres of  $H_2$  and  $H_2O$  and of  $CO$  and  $CO_2$  at practically the same temperatures, whereas in oxidizing atmospheres of air softening did not take place until a considerably higher temperature had been reached, the average difference varying from  $100^\circ$  to  $250^\circ C$ .

Many ashes, however, showed distinct differences in the temperature at which complete deformation of the cones took place in the atmospheres of  $H_2$  and  $H_2O$  and of  $CO$  and  $CO_2$ , as shown in figure 24.

The curves representing average softening temperatures show that the differences gradually increased with an increase of  $Fe_2O_3$ —from  $30^\circ C$ . for an ash with 5 per cent  $Fe_2O_3$  to  $90^\circ C$ . for an ash with 9 per cent  $Fe_2O_3$ . The average difference remained constant until 19 per cent  $Fe_2O_3$  was exceeded when it rapidly decreased to  $20^\circ C$ . and less for ashes having 25 per cent or more of ferric oxide.

Individual samples showed differences both above and below the average curves. The largest observed difference was  $197^\circ C$ . The mean difference for the 48 samples tested was  $66^\circ C$ .

Seemingly, these differences in softening intervals of ash samples in atmospheres of  $H_2$  and  $H_2O$  and of  $CO$  and  $CO_2$  have some relation to the percentage of ferric oxide in the ash, becoming greatest in ashes with an iron oxide content between 9 and 19 per cent.

Silicate mixtures free from iron oxide did not show any material difference, as may be seen in the following results of tests made with standard pyrometric cones:

TABLE 14.—Results of tests to determine softening temperatures of standard pyrometric cones <sup>a</sup> in  $H_2$ - $H_2O$  and  $CO$ - $CO_2$  atmospheres, and in air.

Cone No.	Per cent of $Fe_2O_3$ in Seger-cone formula.	Softening temperature in—			Difference.	
		Atmosphere of equal parts of $H_2$ and $H_2O$ .	Atmosphere of equal parts of $CO$ and $CO_2$ .	Air.	$H_2$ - $H_2O$ and $CO$ - $CO_2$ atmospheres.	$H_2$ - $H_2O$ atmosphere.
		$^\circ C$ .	$^\circ C$ .	$^\circ C$ .	$^\circ C$ .	$^\circ C$ .
06	8.52	1,018	1,026	1,040	+ 8	+22
04	8.54	<sup>b</sup> 1,089	1,062	1,085	-27	- 4
02	8.57	1,119	1,119	1,178	+ 0	+59
1	8.58	1,146	1,164	1,182	-18	+36
2	4.38	1,165	1,170	1,181	+ 5	+16
4	None.	1,221	1,240	1,250	+19	+29
6	None.	1,281	1,292	1,286	+11	+ 5
8	None.	<sup>b</sup> 1,332	1,330	1,366	- 2	+34
10	None.	<sup>b</sup> 1,358	1,340	1,334	-18	-24
12	None.	1,358	1,370	1,367	+12	+ 9

<sup>a</sup>Manufactured by Edward Orton, jr., Columbus, Ohio.

<sup>b</sup>Average of closely checking duplicate determinations.

The average softening-point curves in figure 24 show clearly the effect of increasing percentages of iron oxide in lowering the softening temperatures of coal ashes in reducing atmospheres.

This relation was most clearly indicated in tests with an atmosphere of hydrogen and water vapor, the average softening-point curve dropping from  $1,310^{\circ}$  to  $1,120^{\circ}$  C. with an increase of  $\text{Fe}_2\text{O}_3$  from 5 to 60 per cent. In an oxidizing atmosphere of air the average softening points for the same ashes dropped only from  $1,400^{\circ}$  to  $1,340^{\circ}$  C. Hence iron oxide in the ferric form or as magnetite is not to be regarded as having any marked effect in lowering the fusibility of a coal ash. It is only when the conditions are such as to reduce the iron component of a slag to the ferrous form that its effect becomes marked in lowering the temperature of fusion.

All the cones fused in air were strongly magnetic. Those fused in the  $\text{CO-CO}_2$  atmosphere were mostly nonmagnetic, although a considerable proportion gave evidence of weakly magnetic properties when suspended in the field of a strong electromagnet. In no fused cone was any metallic iron detected under the microscope by the copper sulphate test.

The cones fused in the  $\text{H}_2\text{-H}_2\text{O}$  atmospheres were all nonmagnetic except some of those containing more than 40 per cent ferric oxide, which showed traces of metallic iron.

At first thought it would appear that a  $\text{CO-CO}_2$  atmosphere should unquestionably be accepted as the proper laboratory medium for making fusion tests, as it comprises the principal constituent gases that control slag formation in the fuel bed. There is, however, some difficulty in developing a satisfactory laboratory furnace in which a definite standard concentration of  $\text{CO}$  and  $\text{CO}_2$  can be maintained at temperatures covering the entire range of fusion temperatures of coal ash. For instance, the furnace used in the tests was limited to a maximum temperature of  $1,400^{\circ}$  C. At higher temperatures the silica tube rapidly crystallized and became permeable to gas. As refractory materials are generally permeable to gases at high temperatures, rapid gas currents would be necessary to maintain any definite atmosphere surrounding the cone.

A further seeming objection to the  $\text{CO-CO}_2$  atmosphere is the slowness of the reducing and slagging reactions as shown in the experiments made in this atmosphere; approximate equilibrium seemed to be attained more rapidly in the  $\text{H}_2\text{-H}_2\text{O}$  atmosphere. It was therefore decided to extend the tests with an atmosphere of hydrogen and water vapor to temperatures above  $1,400^{\circ}$  C., a modified type of molybdenum furnace being designed for this purpose.

### MODIFIED MOLYBDENUM FURNACE AND SATURATOR FOR SOFTENING-POINT DETERMINATIONS IN $H_2$ - $H_2O$ ATMOSPHERE.

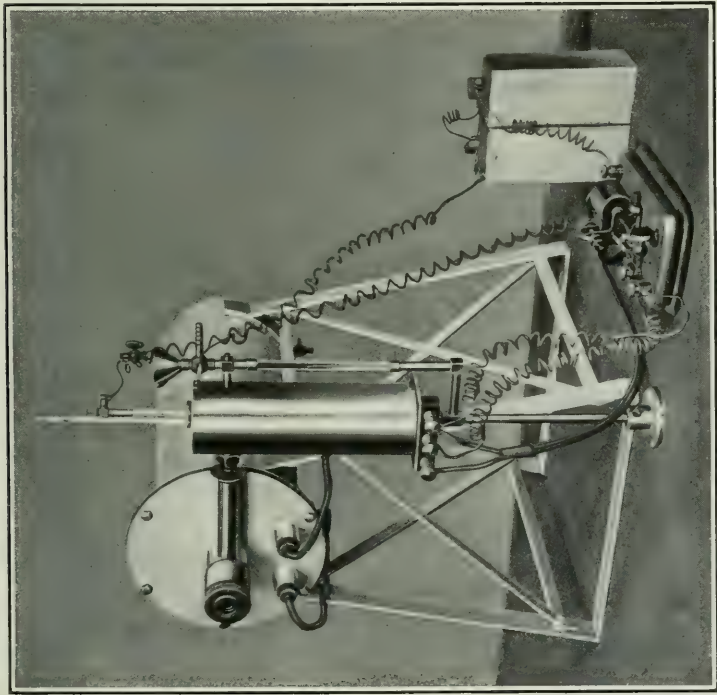
In the experiments previously described the ash cone was heated in a glazed vitreosil tube, through which a current of hydrogen and water vapor was passed continuously. The tube was heated in a horizontal platinum-wire resistance furnace. This apparatus, although satisfactory for the more fusible ashes such as were studied in the former experiments, is not adapted to routine work in which samples softening at temperatures above  $1,400^\circ$  C. may be encountered. A molybdenum-wire resistance furnace was therefore designed in which the entire atmosphere inside the gas-tight sheet-iron jacket could be controlled within the required limits of hydrogen and water vapor (30 to 70 per cent water vapor), thus obviating the necessity of a gas-tight refractory tube.

Preliminary tests, in which molybdenum wire was heated to  $1,400^\circ$  C. in various mixtures of hydrogen and water vapor, showed little oxidation of molybdenum in mixtures containing 60 per cent water vapor; at 70 per cent water vapor a slight superficial oxidation was noted, which was little greater at 90 per cent water vapor. Heating even in 100 per cent water vapor to  $1,400^\circ$  C. caused only a thin surface coating of light-colored oxide. On heating in air the metallic molybdenum was completely oxidized at  $1,100^\circ$  C. From these experiments it appeared that no material trouble from oxidation of the molybdenum heating element would be experienced in an atmosphere of equal parts of hydrogen and water vapor within the temperature limits required for softening most coal ashes, at least those containing over 7 per cent ferric oxide, which fuse at a temperature less than  $1,500^\circ$  C. For ashes that soften at a temperature higher than  $1,500^\circ$  C., it is permissible to run pure hydrogen through the furnace, as the iron oxide content is so low as to have little effect on the fusibility.

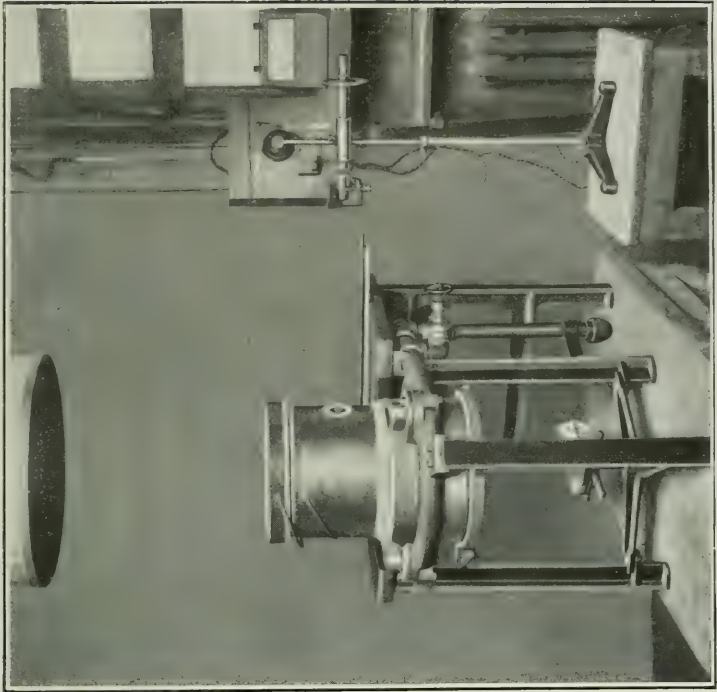
#### DESCRIPTION OF FURNACE AND SATURATOR.

The furnace and saturator are shown in Plate IV, A. The details are given in figures 23 and 27. The furnace consists in part of an outer shell of No. 14 B. & S. gage sheet iron, 7 inches in diameter and 11 inches long, autogenously welded, gas-tight at the seams, and having at the front a circular 1-inch flange perforated for six equally spaced bolts. Between this flange and the circular end plate, both of which are made of  $\frac{1}{4}$ -inch sheet iron, is placed an asbestos gasket,  $\frac{1}{16}$  inch thick, painted with a thick mixture of powdered graphite and glycerin. This end plate and flange are drawn together sufficiently tight to produce a gas-tight connection. The mixture of hydrogen and water vapor enters the shell through a  $\frac{1}{8}$ -inch horizontal



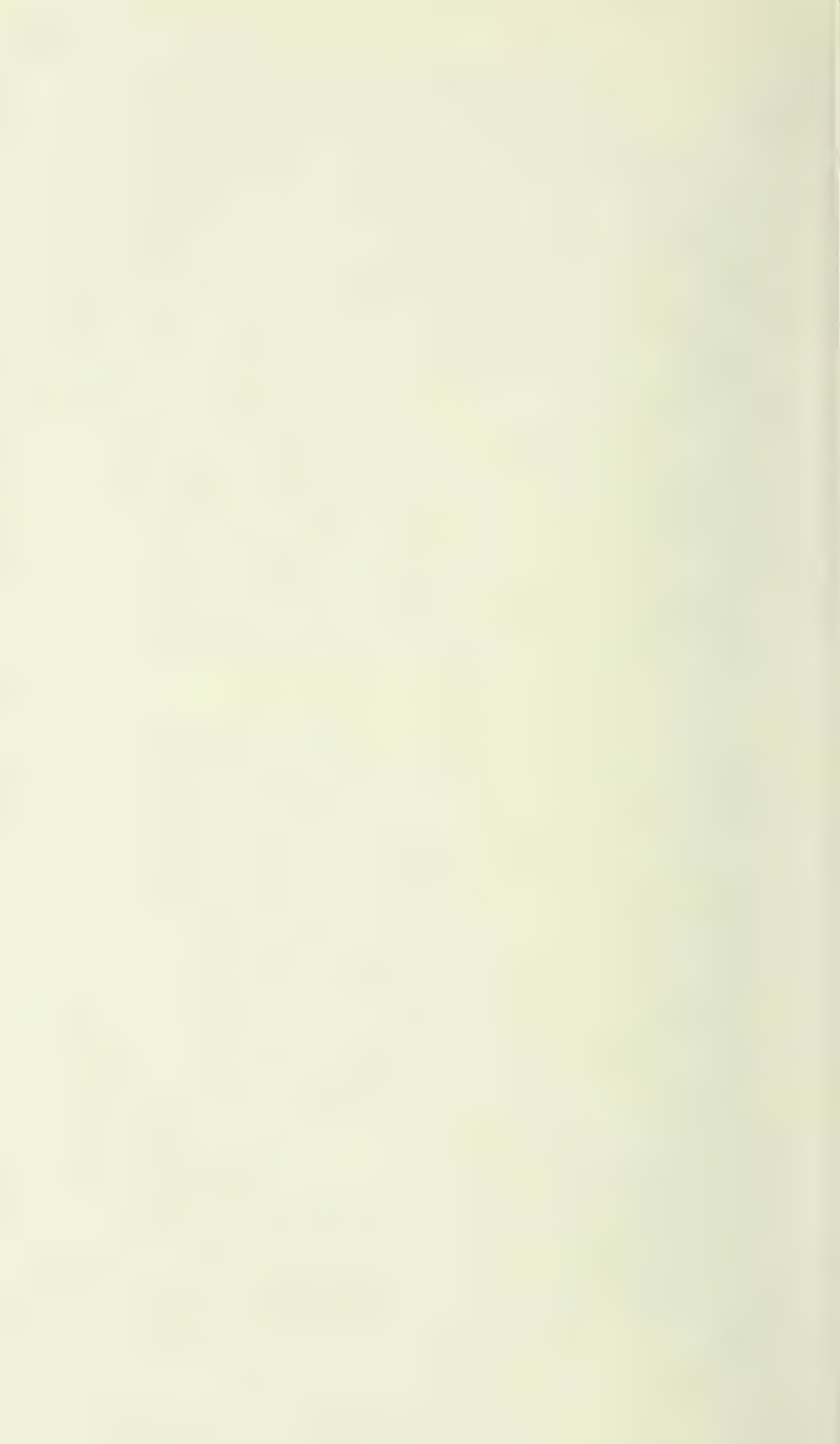


A. MOLYBDENUM FURNACE AND SATURATOR.



B. NO. 3 MELTER'S FURNACE ARRANGED FOR FUSING TESTS.





pipe, threaded into a  $1\frac{1}{4}$ -inch iron pipe serving as an observation tube, which in turn is threaded into the center of the front end plate. A vertical  $\frac{1}{8}$ -inch iron pipe with a brass stopcock threaded into

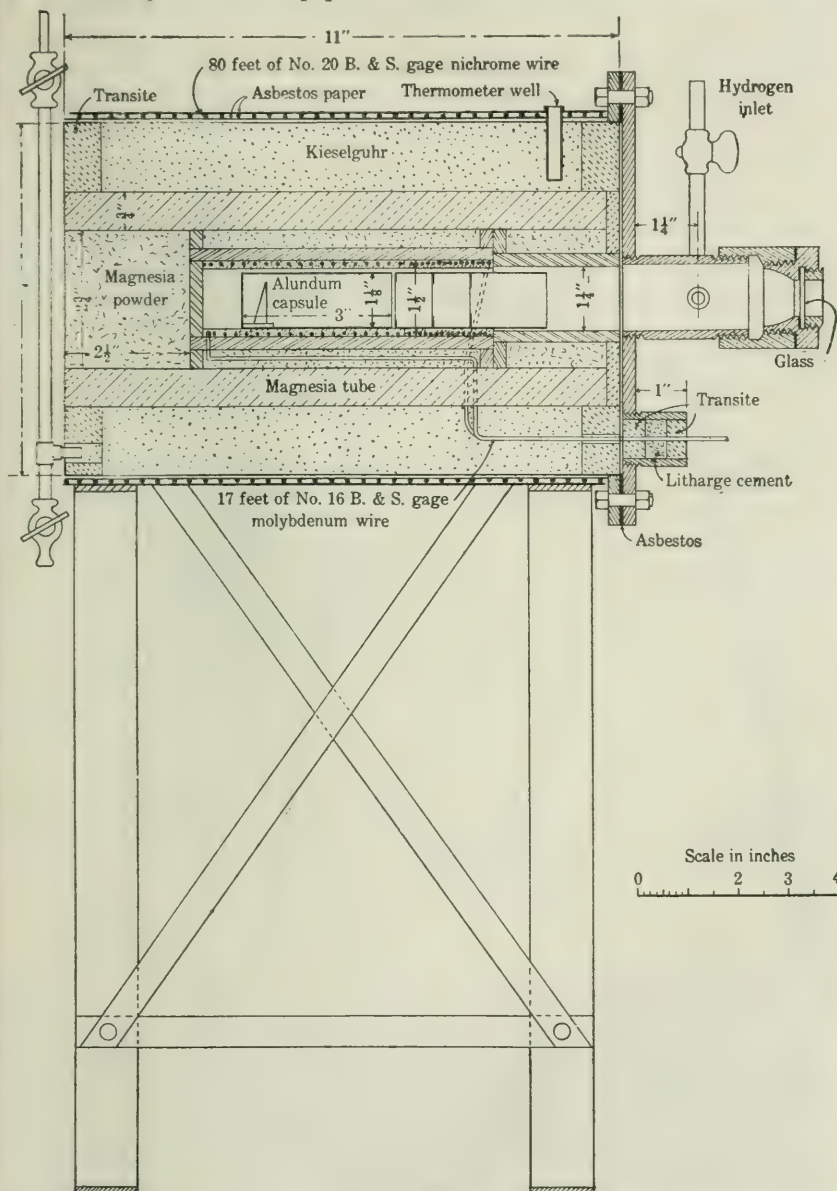


FIGURE 26.—Vertical longitudinal section through molybdenum furnace No. 3.

the top of the observation tube serves as a by-pass around the saturator for admitting pure hydrogen to the furnace. The free end of the observation tube carries a brass sleeve into which is threaded

a brass cap bearing on an asbestos gasket, as shown in figure 26. The cap is fitted with a glass window, through which the temperature is read optically. The glass is held between two asbestos gaskets by

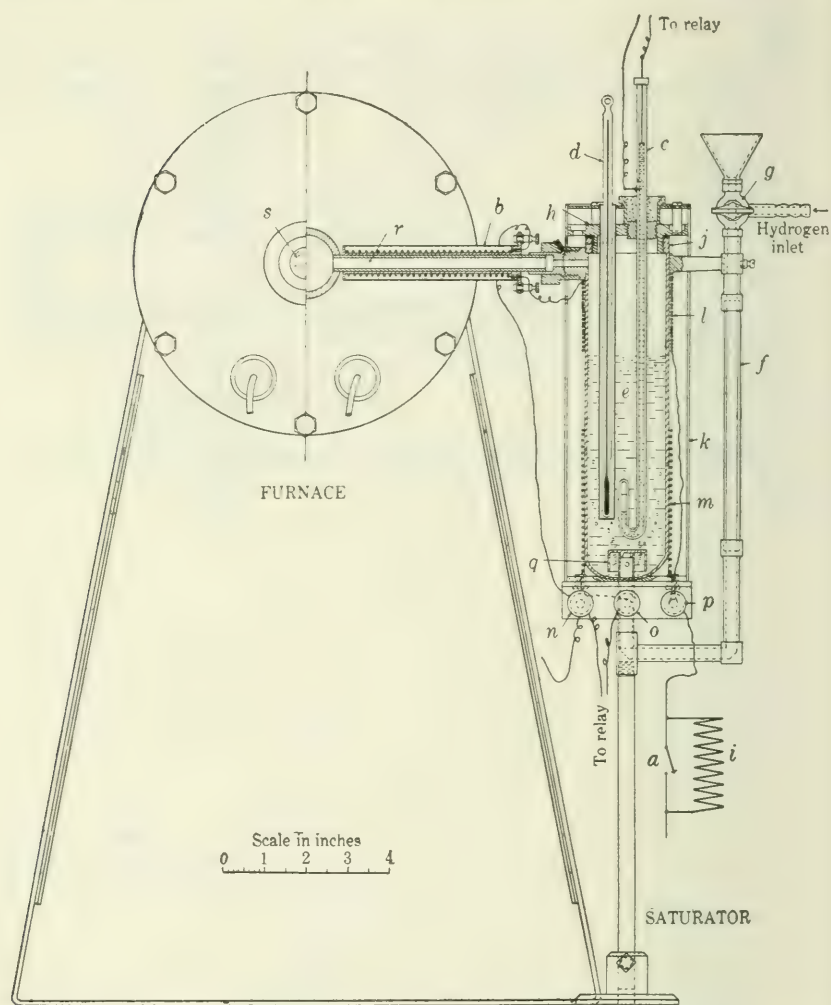


FIGURE 27.—Front elevation of molybdenum furnace No. 3 and vertical section through saturator. *a*, Switch for cutting out resistance *i*; *b*, metal jacket covering superheater; *c*, vapor-pressure thermoregulator; *d*, thermometer; *e*, water in saturator; *f*, glass gage; *g*, brass three-way cock; *h*, cover of saturator; *i*, resistance coil; *j*, body or saturator; *l*, upper heating coil of saturator for continuous duty, *m*, lower heating coil of saturator for intermittent duty; *n*, *o*, *p*, binding posts; *q*, perforated baffle for breaking up hydrogen into small bubbles; *r*,  $\frac{1}{2}$ -inch iron pipe wound with asbestos and nichrome wire to prevent condensation of water vapor; *s*, glass window for observing cones.

a threaded brass ring. To insert a cone in the furnace, the entire cap is unscrewed from the brass sleeve. The furnace is supported in an

iron frame so that its center is about 17 inches above the table, which is a convenient height for optical measurements of temperature.

The heating element consists of 17 feet of molybdenum wire, No. 16 B. & S. gage, wound upon the inside of an alundum tube,  $1\frac{1}{2}$  inches in internal diameter, 6 inches long, and closed at one end by an alundum disk cemented in with alundum cement. The wire is wound 6 turns to the inch except at the front, where compensation for radiation is obtained by winding 10 turns on the first inch. This tube, carrying the coil of molybdenum wire, when placed in position, lies in the axis of the cylindrical shell,  $2\frac{1}{2}$  inches from the rear end and  $2\frac{1}{2}$  inches from the front end, measured to the plane of the flange. The heated alundum tube is supported by being placed within a magnetic tube  $2\frac{3}{4}$  inches in internal diameter and  $10\frac{3}{4}$  inches long. The magnesite tube prevented deformation of the alundum tube at high temperatures. The narrow annular space between the tube carrying the molybdenum coil and the magnesite tube is filled with light calcined magnesia powder, free from carbonate.

The magnesite tube is provided with two slots at the front end for leading out the terminals of the molybdenum coil. At the front end the cylindrical heating chamber is continued along the axis by a short alundum tube,  $1\frac{1}{4}$  inches in internal diameter. The  $1\frac{1}{4}$ -inch annular space between the magnesite tube and the outer iron shell is filled with previously ignited kieselguhr (infusorial earth). The magnesite tube is supported at the ends by rings of "transite," 1 inch thick. The rear terminal of the heating coil passes between the alundum tube and the magnesite tube to the front end of the heating coil, through a slot in the magnesite tube, and out of the furnace through a  $\frac{3}{4}$ -inch pipe, 1 inch long, threaded into the front plate. The front terminal passes through a similar slot in the magnesite tube and out of the furnace. The positions of these terminals can be better seen by reference to figure 27, which shows the front of the furnace.

The leads are centered in the pipes by an outer and an inner disk of "transite," between which is a layer of litharge cement. (See fig. 26.) This makes a gas-tight arrangement, which is not affected by the temperature to which the shell is subjected.

In order to obtain a background suitable for measuring the temperature of the test piece with accuracy, a thin alundum disk is cemented in at the rear end of the tube carrying the heating coil. The space back of this disk is provided with light calcined magnesia powder. The heating space, which is  $1\frac{1}{4}$  inches in diameter and 6 inches long, affords a uniformly heated part approximately 3 inches long. The ash cone is placed in a No. 5811 alundum extraction thimble,  $1\frac{1}{8}$  inches by 3 inches. When this is to be inserted the



brass cap on the observation tube is taken off and the thimble is pushed back about 1 inch beyond the center of the heating coil. Another alundum capsule having two or three diaphragms is then introduced to minimize radiation loss. Under normal conditions the cone is barely visible against the background.

In order to heat the outer shell of the furnace rapidly to a temperature at which no water can condense from the atmosphere of hydrogen and water vapor in the furnace, 110 feet of No. 20 B. & S. gage nichrome wire, about five turns per inch, is wrapped around the outside of the furnace. This length and size of wire will allow three amperes to flow when the wire is connected directly across a 220-volt circuit and will heat the outer shell to a temperature of 90° C. in 15 minutes, which will prevent the condensation of moisture from the  $H_2$ - $H_2O$  atmosphere.

The wire is insulated from the furnace by first wrapping the iron shell with thin asbestos paper. The resistance wire is wound on this paper and fastened at each end of the furnace with asbestos cord. Another sheet of asbestos paper is then wrapped around the furnace to cover the resistance wire, as shown in figure 26.

The desired mixture of hydrogen and water vapor is obtained by bubbling hydrogen through water held at the proper temperature. The exact temperature depends on the prevailing barometric pressure and the proportions of water vapor and hydrogen desired. A temperature of 81° C. is required for a mixture containing equal parts of water vapor and hydrogen.

The saturator is constructed of brass and its temperature is controlled automatically by a vapor-pressure thermo regulator. The water in the saturator is heated by a coil of nichrome wire wound around the saturator and connected in series with a relay which is operated by the thermo regulator. Complete details of this saturator and an earlier form of the molybdenum furnace have been published in a previous report.<sup>a</sup> The method of operating the present form of molybdenum furnace in making a softening-temperature determination is essentially the same as described therein.

Similar results were obtained on repeating in this furnace softening-point determinations of a number of ashes that had been tested previously in the silica-tube furnace, shown in figure 17 (p. 51).

This furnace when operated as described above gave softening temperatures that were usually duplicated within the known errors of observation (about 25° C.). The fused cones from coal ash containing less than 50 per cent ferric oxide did not show any material degree of magnetism in the field of a strong electromagnet, indicating

<sup>a</sup> Fieldner, A. C., and Feild, A. L., A new method and furnace for the determination of the softening temperature of coal ash under fuel-bed conditions: Jour. Ind. and Eng. Chem., vol. 7, 1915, p. 829.

a reduction of the iron present in the ash to the ferrous state, but not to metallic iron. This condition corresponds to the minimum softening temperature, for the determination of which the furnace was designed. Most of the determinations in hydrogen and water vapor given in Table 13 were determined in this furnace, and it was given a thorough trial in routine work and in continuing the study of factors affecting the minimum softening temperature in atmospheres of hydrogen and water vapor.

#### EXPERIMENTS WITH VERTICAL AND HORIZONTAL PLACING OF CONES IN DETERMINATION OF SOFTENING TEMPERATURE.

Ricketts,<sup>a</sup> of the New York Edison Co., has modified the usual Seger-cone method of ash-fusing determinations by placing the cone in a horizontal position. Marks also prefers this method as being more sensitive and as giving indications which can be duplicated more accurately than the usual vertical method.<sup>b</sup> His objection to the vertical position was based on the seeming separation of a more fusible and very fluid constituent in certain ashes, which ran downward to the base of the cone and left the apex seemingly unchanged in a vertical or slightly inclined position until at a higher temperature the apex also melted.

On the other hand, Palmenberg<sup>c</sup> states that "this difficulty does not seem to present itself when the cones are made long and thin, at least not to the extent of interfering with the tests. If the ash is thoroughly ground and mixed, a complete fusion of the whole mass should take place."

A large number of determinations made with vertical cones in the Bureau of Mines laboratory did not show any separation of a fluid constituent when the determination was made in a mixture of equal parts of hydrogen and water vapor or a similar mixture of CO and CO<sub>2</sub>, nor has there been any such separation of a low-melting slag in any coal ash containing less than 50 per cent ferric oxide when the determination has been made in the purely oxidizing atmosphere of a platinum-wire resistance furnace. However, in some coal ashes, as fused in several types of carbon and graphite resistance furnaces containing a strongly reducing atmosphere of carbon monoxide and

<sup>a</sup> Ricketts, E. B., Discussion of L. S. Marks's paper on "The clinkering of coal": Jour. Am. Soc. Mech. Eng., vol. 37, 1915, p. 213; Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 830-833.

<sup>b</sup> Marks, L. S., The clinkering of coal: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 806-807; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, p. 206.

<sup>c</sup> Palmenberg, O. W., Discussion of paper on "Clinkering of coal," by L. S. Marks: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, p. 825; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 211-212.

nitrogen, certain phenomena observed were in general similar to the observations of Marks. These cones, as shown in Plate I, *C* (p. 42), did not deform in the usual manner. The upper part of the skeleton of a fused cone contained a considerable quantity of metallic iron and consisted simply of the unchanged original apex of the cone. The thickened lower part was a thin-shelled bubble of fused slag. Hence the authors consider that this phenomenon was not due to a separation of fusible constituents, but merely to an earlier fusion of the thick part of the cone. The thin part was rendered less fusible more rapidly than the thick part by reduction of iron oxide to the metallic iron.

Although the objection cited by Marks to the use of the vertical position does not apply to softening-temperature determinations made in an oxidizing atmosphere nor in a mixture of equal parts of hydrogen and water vapor or of carbon monoxide and carbon dioxide, a number of fusibility determinations with cones placed horizontally have been made to determine whether horizontal placing in itself possessed any features that would make such placing preferable in routine testing to the usual vertical placing. The effect of inclination of the ash cone on the softening temperature has been shown previously for three different degrees of inclination, viz,  $25^{\circ}$ ,  $35^{\circ}$ , and  $45^{\circ}$  from the vertical. Although the effect of the  $25^{\circ}$  inclination was negligible, the  $35^{\circ}$  and  $45^{\circ}$  inclinations gave average softening points about  $20^{\circ}$  lower than those obtained with cones in the vertical position. Undoubtedly the horizontally mounted cone should give still lower values. Marks<sup>a</sup> made a series of tests with cones placed horizontally and vertically in a Meker furnace having an oxidizing atmosphere. He found that the deformation temperature of a horizontal cone was always lower than of a vertical cone. The difference varied from  $5^{\circ}$  to  $50^{\circ}$  C. and was less for the more fluid melts. In making the tests with the cones in the horizontal position he took as the "down point" the temperature at which the tip of the cone pointed vertically downward.

#### METHOD OF CONDUCTING EXPERIMENTS.

Tests with cones in both the horizontal and the vertical position were made in the new type molybdenum furnace with an atmosphere containing equal parts of hydrogen and water vapor. The cones were three-sixteenths of an inch wide at the base by 1 inch high, and were heated at the usual rate of  $5^{\circ}$  and  $2^{\circ}$  C. per minute.

<sup>a</sup> Marks, L. S., The clinkering of coal: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, p. 810; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, p. 206.



In tests with the cone in the horizontal position the cone was placed at right angles to the axis of the furnace, a position favoring easy observation of the softening process. The cone was supported by placing its base in a notch cut in the wall of an alundum capsule, which fitted snugly within the larger capsule used in the tests in which the cone was placed vertically. The small inner capsule was sliced longitudinally slightly above its axis, and the upper "half" was removed. Thus, the cone could be placed in position in the notch and secured by a fillet of the usual infusible mixture of kaolin and alumina. After the cone had dried, the capsule could be placed within the larger capsule without disturbing the mounted cone.

It was found just as difficult to define the down points of horizontal cones as to fix those of vertical cones. Some of the ash cones formed globules at the tips and shortened considerably in length before the axes bent appreciably; the tips of others bent vertically for only a short distance toward the bases; in a third type, the tip of the cone did not become vertical until the larger part of the cone axis was vertical or nearly vertical. In this work, therefore, the "down point" or softening point of cones placed horizontally is defined as the temperature at which a vertical line may be drawn through the tip of the cone or the center of the globule formed at the top, and a point on the axis of the cone midway between the tip and the base. Likewise a  $45^\circ$  deformation for horizontal cones is reached when a similar line makes an angle of  $45^\circ$  with the vertical.

The "softening point" or "down point" for vertical cones is the temperature at which the tip of the bent cone touches the base, or, if it fails to bend, the temperature at which the cone settles into a more or less spherical lump, which may or may not have swelled.

#### RESULTS OF EXPERIMENTS.

The results of softening-temperature determinations of seven synthetic mixtures and eight coal ashes with cones placed both vertically and horizontally are given in Table 15. The synthetic mixtures were made from pure North Carolina kaolin, ferric oxide, and calcium carbonate. The analyses of the mixtures and the ash samples are given in Table 16.



TABLE 15.—*Results of softening-temperature tests, showing relative effects of vertical and horizontal placing of cones.*

[Values in centigrade degrees.]

Sample No.	Cones placed vertically.			Cones placed horizontally.			Difference.		
	Temperature of initial deformation.	Down point	Softening interval.	Temperature of initial deformation.	Down point.	Softening interval.	Temperature of initial deformation.	Down point.	Softening interval.
M10.....	1,183	1,209	26	1,135	1,170	35	48	39	- 9
M23.....	1,103	1,105	2	1,072	1,113	41	31	-8	- 39
M33.....	1,063	1,086	23	1,053	1,063	10	10	23	13
M20.....	1,204	1,403	199	1,191	1,204	15	13	199	184
M19.....	1,401	1,408	7	1,216	al, 394	178	185	14	-171
M4.....	1,431	1,431	0	1,421	al, 428	7	10	3	- 7
M28.....	1,340	1,426	86	1,242	1,340	98	98	86	- 12
20913.....	1,164	1,202	38	1,113	1,177	64	63	18	- 45
				1,089	1,191	102			
				1,113	1,158	45			
19472.....	1,153	1,204	51	1,113	1,165	52	40	42	2
				1,051	1,113	62			
20914.....	1,080	1,116	36	1,058	1,096	38	25	11	- 14
16584.....	1,291	1,351	60	1,177	1,212	35	114	139	25
20915.....	1,057	1,099	42	1,044	1,063	19	13	36	23
15842.....	1,350	1,409	59	1,145	1,291	146	205	118	- 87
19160.....	1,504	1,551	47	1,482	al, 551	69	22	0	- 22
20233.....	1,320	1,378	58	1,127	al, 362	235	193	16	- 17
Average.....			49			70	71	49	- 22

a Cone did not bend vertically downward, but simply shortened up to a globule in the same manner as did cones mounted vertically.

## Temperatures at Which Swelling of Cones Became Noticeable.

Sample No.	Cone placed vertically.	Cone placed horizontally.
	° C	° C
M33	1,063	1,058
20913	1,164	1,130
19472	1,153	1,165
16584	1,291	1,191
20915	1,057	1,055

TABLE 16.—*Results of analyses of coal ashes and synthetic mixtures tested with the cones used in the vertical and in the horizontal position.*

Sample No.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SO <sub>3</sub> .	Total.
	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
M10.....	32.6	27.9	32.7	.....	6.9	0.04	.....	.....	.....	100.1
M23.....	32.0	27.4	40.7	.....	.03	.04	.....	.....	.....	100.2
M33.....	38.1	21.4	35.5	1.3	.7	.7	0.5	2.1	0.3	100.6
M19.....	38.3	32.9	28.8	.....	.04	.05	.....	.....	.....	100.1
M4.....	45.6	39.1	5.9	.....	9.6	.1	.....	.....	.....	100.3
M28.....	53.3	29.9	9.7	1.8	.9	.9	.6	2.9	.4	100.4
20913.....	43.3	31.4	13.6	1.2	4.2	1.4	.6	2.9	1.4	100.0
19472.....	38.4	24.2	22.4	1.1	7.7	.9	.3	1.9	3.8	100.7
20914.....	35.7	23.5	32.9	1.2	3.2	1.1	.3	1.1	.5	99.5
16584.....	54.8	29.2	6.9	1.8	1.4	.6	1.9	2.1	1.0	99.7
20915.....	12.3	12.2	69.7	.4	3.9	.7	.3	.6	.2	100.3
15842.....	55.8	33.5	5.0	.9	1.5	.7	.5	2.2	.1	100.2
19160.....	54.2	33.0	7.4	.....	1.1	.5	1.0	1.9	.9	100.0
20233.....	47.3	34.6	9.8	1.8	1.3	.4	2.1	2.5	.1	99.9

As would be expected, the cones, placed horizontally, had lower softening points than those placed vertically, the differences, varying with the viscosities of the melting eutectics, being  $0^{\circ}$  to nearly  $200^{\circ}$  C. The average difference for the 15 samples tested was  $49^{\circ}$  C. Owing to the greater force acting on the cross section of a cone placed horizontally, it begins bending at a comparatively early stage of the melting-

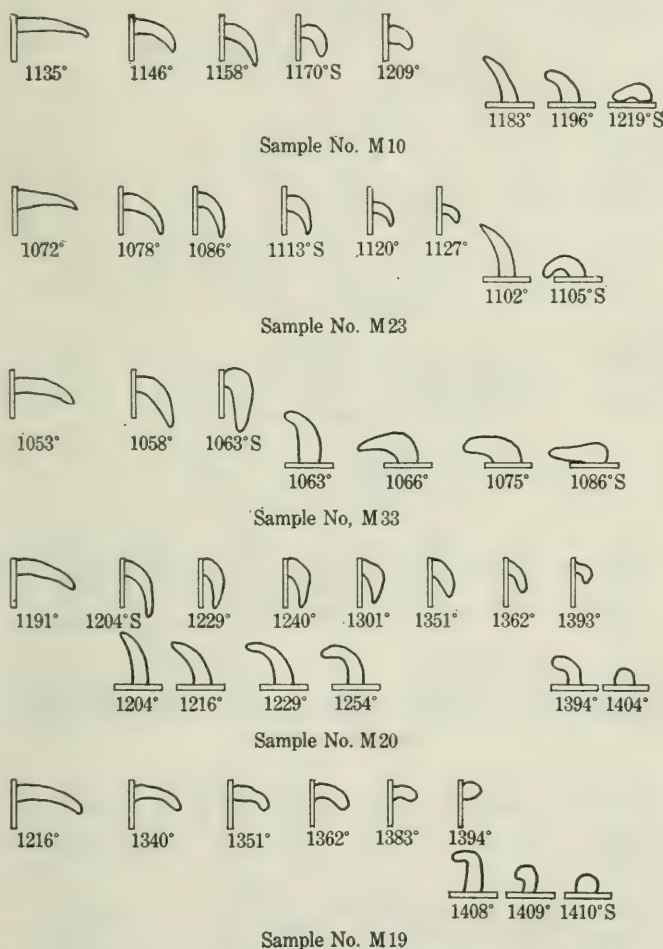


FIGURE 28.—Appearance of vertical and horizontal ash cones at various stages of softening—samples M10, M19, M20, M23, and M33.

ing process, so that the softening interval is usually somewhat longer than that of a cone placed vertically.

Figures 28, 29, and 30 show the appearance of the horizontal and the vertical cones at various stages of softening.

Some of these samples, as M23, M33, M4, 20914, 19160, and 20915, showed for either position final deformation points that were not far

apart on the temperature scale, whereas other samples, as M20, 15842, and 16584, reached the so-called "down point" for the horizontal position at a temperature of 100° to 200° C. below the "down point" for the vertical position. In particular, the horizontally placed cone

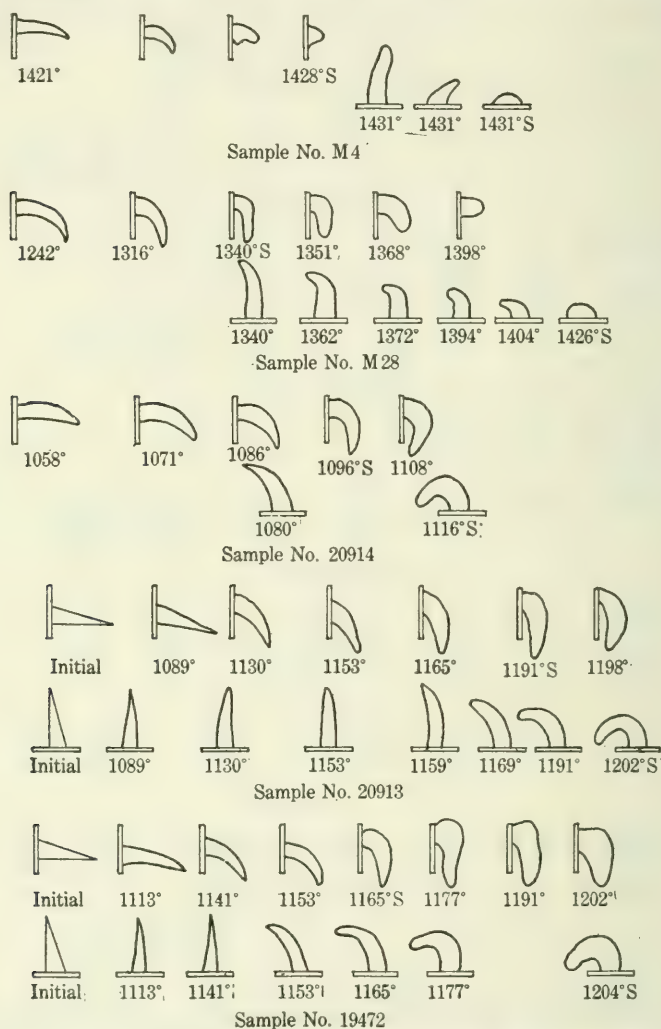


FIGURE 29.—Appearance of vertical and horizontal ash cones at various stages of softening—samples M4, M28, 19472, 20913, and 20914.

from sample 16584 reached the "down point" before any visible deformation took place in the cone placed vertically.

This difference in behavior illustrates the extremely variable character of the fusion process in coal ashes. The sudden formation of a relatively large proportion of fluid eutectic would cause the cone to

deform rapidly in either position and at similar temperatures. Sample M4 is an especially good example of such a mixture. The softening interval in either position was not over  $7^{\circ}$  C., and the down point for either position was practically the same.

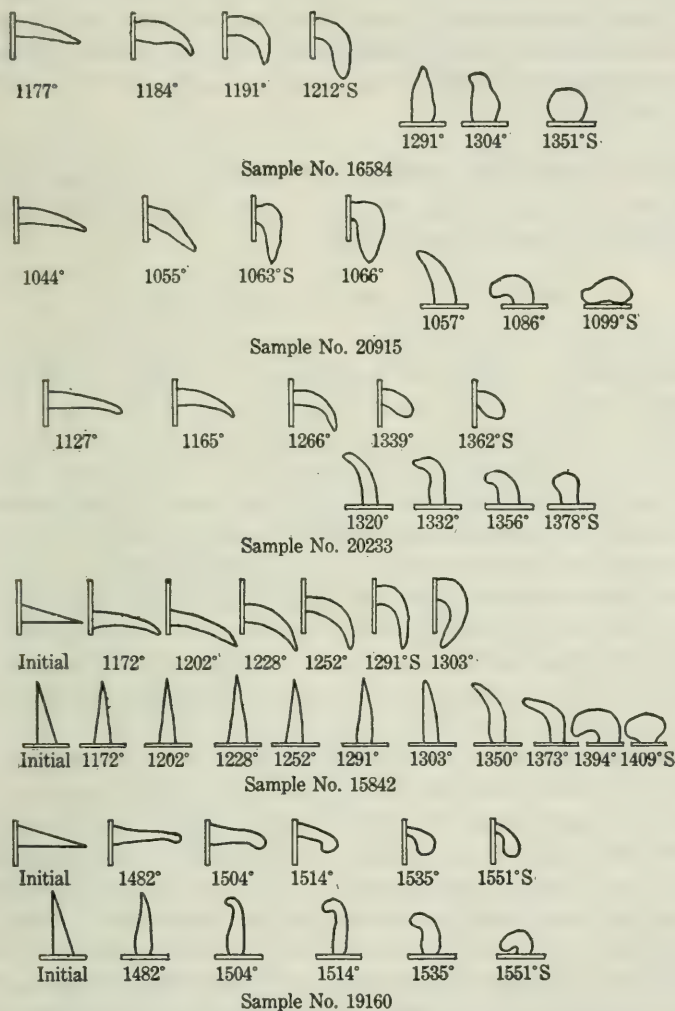


FIGURE 30.—Appearance of vertical and horizontal ash cones at various stages of softening—samples 15842, 16584, 19160, 20233, and 20915.

Sample M19 represents another type of fusion characterized by certain peculiar relations between surface tension and viscosity. The cone, whether in the horizontal or the vertical position, fused to a nearly spherical globule without bending in the usual manner.

It is evident that no fixed difference can be assigned between results obtained by vertical mounting of the cones as compared with hori-



zontal mounting, nor is there any apparent advantage as regards closeness of duplication inherent in either method. The principal difference is that the down point of a vertical cone indicates a temperature at which the melting ash has reached a greater degree of fluidity than that indicated by the deformation point of a horizontal cone. This is undoubtedly a point in favor of the vertically mounted cone, as, according to furnace data thus far accumulated, clinker does not cause serious trouble unless it becomes sufficiently fluid to flow in the fuel bed.

### **EFFECT OF DEXTRIN BINDER OR RESIDUAL CARBON ON SOFTENING TEMPERATURE OF ASH, AND ITS RELATION TO INTUMESCENCE OF SOFTENING CONE.**

#### **SWELLING OF MELTING ASH CONES.**

Attention has been called to the pronounced vesicular structure of ash cones fused in a hydrogen atmosphere. A similar decided "bleb" structure, accompanied in many instances by considerable intumescence, has been noted in the majority of ash samples that were fused in mixtures of hydrogen and water vapor. Indeed, some degree of swelling of the softening cone is characteristic of fusions made in any atmosphere containing material proportions of hydrogen. Swelling and intumescence, but to a distinctly less degree, occur also in atmospheres containing carbon monoxide. In atmospheres of air, water vapor, or carbon monoxide intumescence occurs rarely. It appears, then, that intumescence occurs most generally under conditions favoring the reduction of the original ferric oxide of the coal ash.

As other possible causes of swelling there may be considered: (1) Presence of substances that develop an appreciable vapor pressure at the melting temperature; (2) decomposition of sulphates, sulphides, and carbonates; and (3) oxidation of unburned particles of coke in the interior of the cone. Cause 3 especially should receive careful consideration, as even after prolonged heating in a muffle at 750° C. coal ash sometimes contains minute particles of coke, which are visible under the microscope. Unburned dextrin or other organic binding materials may also under certain conditions cause the melting cone to swell.

### **EXPERIMENTS TO DETERMINE EFFECT OF UNBURNED CARBON IN ASH ON SOFTENING OF CONE.**

In order to determine the effect of carbonaceous binder and unburned carbon on the fusion of cones, several samples of various types of ash were reground to a fine powder and reheated five or six

hours in an electric muffle at approximately 800° C. When, after this treatment, the ash still showed possible traces of coke, it was again ground in the mortar and heated for several hours in a Meker muffle furnace at a temperature of 900° to 1,000° C., until microscopic examination showed complete absence of all traces of coke. Some of these ashes were slightly "fritted" at this temperature so that repulverization was necessary before molding the cones. The results of analyses of these samples are presented in Table 17 following:

TABLE 17.—*Results of analyses of coal ashes used in experiments to determine influence of carbon on the softening temperature and the intumescence of ash cones.*

Sample No.	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> . <sup>a</sup>	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .	CaO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	SO <sub>3</sub> .
	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>	<i>P. ct.</i>
86.....	31.0	22.7	42.8	.....	2.1	0.5	.....	.....	0.6
101.....	42.1	32.7	19.3	.....	2.5	.6	0.9	1.3	1.1
15.....	54.1	24.8	9.4	2.3	4.0	1.4	1.0	.8	2.8
9.....	54.8	27.0	7.0	1.3	4.3	1.7	.3	3.1	.6
102.....	56.9	27.8	9.3	.....	1.6	1.1	1.1	1.3	.9
103.....	52.2	33.4	7.9	.....	1.9	.6	1.5	1.4	.9
7.....	54.1	34.7	4.5	1.5	1.2	.9	.6	2.5	.2

<sup>a</sup> Includes P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub> where not separately determined.

Seven samples prepared in this way were made into three series of cones, as follows: The cones in series 1 were molded with distilled water only, so that no carbonaceous matter could be present; the cones in series 2 were molded in the usual manner with a 10 per cent dextrin solution; the cones were placed in the furnace without previous burning of the dextrin; the cones in series 3 were molded with 10 per cent dextrin solution, after an amount of sugar carbon equal to 10 per cent of the mixture had been added to the ash; these cones were also placed directly in the furnace without any previous ignition.

One series of softening-temperature tests was made in an atmosphere of equal parts of hydrogen and water vapor, in the furnace shown in Plate IV, A (p. 74); another series of tests covering ashes that softened under 1,400° C. was made in an atmosphere containing equal parts of CO and CO<sub>2</sub>, in the furnace shown in Plate II (p. 46). The softening temperatures and the degree of intumescence observed are given in Table 18 following.

TABLE 18.—*Results of tests to determine influence of carbon on the softening temperature and on the intumescence of ash cones.*

Rate of temperature increase 5° C. per minute until initial softening of cone; then 2° C. per minute until cone melted.]

## ATMOSPHERE OF EQUAL PARTS OF HYDROGEN AND WATER VAPOR.

Lab. No.	Softening temperature.			Differences.		Degree of intumescence.		
	Series 1— cone molded with distilled water only	Series 2— cone molded with 10 per cent dextrin solution.	Series 3— ash con- taining 10 per cent sugar carbon and dextrin.	Between results of series 1 and 2.	Between results of series 1 and 3.	Series 1— distilled water only.	Series 2— 10 per cent dextrin solution.	Series 3— 10 per cent sugar car- bon and dextrin.
	° C.	° C.	° C.	° C.	° C.			
22665.....	1,080	1,072	1,060	- 8	-20	Marked....	Marked....	Marked.
19159.....	1,146	1,182	1,177	+36	+31	.....do.....	.....do.....	Do.
16585.....	1,278	1,291	1,254	+13	-24	Slight.....	Slight.....	Slight.
15848.....	1,325	1,328	1,326	+ 3	+ 1	Moderate...	Moderate...	Moderate.
19155.....	1,345	1,351	1,384	+ 6	+39	Slight.....	Slight.....	Do.
19161.....	1,500	1,500	1,512	0	+12	.....do.....	.....do.....	Slight.
15846.....	1,600	1,605	1,596	+ 5	- 4	.....do.....	.....do.....	Do.
Average.				+ 8	+ 5			

ATMOSPHERE OF EQUAL PARTS OF CO AND CO<sub>2</sub>.

22665.....	1,077	1,077	1,085	0	+ 8	None.....	None.....	Very slight.
19159.....	1,350	1,350	1,320	0	-30	.....do.....	.....do.....	Do.
16585.....	1,301	1,292	1,279	- 9	-22	.....do.....	.....do.....	None.
15846.....	1,340	1,345	1,320	+ 5	-20	Slight.....	Moderate...	Slight.
Average.				- 1	-16			

It may be concluded from the results of the tests that the puffing or intumescence is not due primarily to the presence of unburned coke or carbon particles in the coal ash. At the rate of heat increase used in the experiments, namely, 5° C. per minute, small amounts of carbon are probably removed from the system by reacting with the gaseous atmosphere before the sintering temperature is reached. In an atmosphere containing oxygen, 50 per cent water vapor, or 50 per cent carbon dioxide, the solid carbon will be removed as carbon monoxide at temperatures below 1,000° C., provided the rate of heating is not too rapid. This conclusion is also corroborated by the experiments of Marks and those of Palmenberg. Marks<sup>a</sup> has shown that ash cones molded with 10 per cent dextrin solution softened in the oxidizing atmosphere of a Meker furnace at practically the same temperature as similar cones molded with distilled water only. The rate of heat increase was 2° C. per minute.

Palmenberg,<sup>b</sup> who also used a Meker furnace, found that as much as 10 per cent carbon had no appreciable effect on the softening tem-

<sup>a</sup> Marks, L. S., The clinkering of coal: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, p. 810.

<sup>b</sup> Palmenberg, O. W., Discussion of Marks's paper, The clinkering of coal: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, p. 824.



perature. A few investigators have reported that traces of carbon left in the ash or the presence of an unoxidized organic binder caused intumescence and abnormal deformation points. However, an analysis of their methods of making softening-point determinations has shown that they invariably heated the cone rapidly—40° to 70° C. per minute. Under these conditions it is quite possible that carbon was not removed by the surrounding gases before the softening temperature was reached.

### MOLYBDENUM FURNACE AS STANDARD FURNACE FOR FUSION TESTS.

The molybdenum furnace was used for a period of one year in routine and in special softening-temperature determinations of coal ash, clays, and similar materials, thus affording an excellent opportunity to pass judgment on its practical usefulness as a standard type of furnace for determining the fusibility of coal ash. Any standard method for the determination of the fusibility of coal ash should answer the following requirements:

- (1) The atmosphere should reduce the iron component of the ash to the ferrous state in which it can exert its maximum fluxing action.
- (2) The method should give consistent and reproducible results when used by different chemists.
- (3) The method should be simple and rapid.
- (4) The furnace should be comparatively cheap and easily operated and repaired with the means available in the ordinary commercial laboratory.

If these criteria be applied to the molybdenum furnace with an atmosphere of hydrogen and water vapor as tried for a year in the Bureau of Mines laboratory, the method may be said to meet requirements 1 and 2, but to fail with respect to requirements 3 and 4.

In recent years the price of molybdenum wire has advanced materially so that the cost of renewing heating elements is a serious item. With temperatures up to 1,450° C. the element is fairly durable, but if the furnace is frequently heated to higher temperatures, as 1,600° C., oxidation by the water vapor causes the molybdenum wire to waste away and eventually burn out.

The replacement of such units, although comparatively unimportant in a laboratory equipped for renewing electric furnaces, is a more serious matter to the busy commercial laboratory. Such laboratories do not have the time nor the means to make the various electrical repairs and adjustments required in the somewhat complicated electrical system of the molybdenum furnace and saturator.

A simple form of gas furnace would be cheaper and more easily repaired; it could also be adapted to making a number of determina-



tions simultaneously. Hence the possibilities of the gas-heated furnace were studied to determine whether the combustion could be so controlled as to produce an atmosphere of approximately constant composition and of the proper reducing character.

## FUSIBILITY OF COAL ASH AS DETERMINED IN GAS FURNACE.

### THEORETICAL CONSIDERATIONS.

As mentioned previously, exceedingly variable results for softening temperature have been obtained in tests made in muffle furnaces. These variations were due to the variable amounts of gas and products of combustion that penetrated the muffle and reacted with the coal ash. Now, if a furnace be constructed with a very porous muffle or one with suitable openings so that the combustion gases have free access to the cones, it should be possible to subject the cones to a reducing atmosphere merely by operating the furnace with a deficient air supply. The proportion of reducing gases in the furnace atmosphere could thus be increased to a certain maximum limit at which combustion slows down to a rate at which the desired temperature can not be attained. If this maximum amount of reducing gas does not reduce the iron constituents of the ash to metallic iron, the most desirable method of operating the gas furnace becomes simple, namely, using the lowest possible proportion of air in the mixture that will sustain the required intensity of combustion.

In the experiments described subsequently no more than traces of metallic iron were ever found under maximum reducing conditions.

### DESCRIPTION OF FURNACE.

An investigation of the various gas furnaces on the market led to the selection of the No. 3 melter's furnace (Pl. IV, *B*, p. 74) of the American Gas Furnace Co. Ricketts<sup>a</sup> has used this furnace for a number of years for determining ash-softening temperatures in the laboratory of the New York Edison Co. This type of pot furnace is especially suitable for fusion determinations in that the burners, three in number, are on a tangent near the base of the furnace, thus producing a rotary flame which completely surrounds the crucible in which the cones are placed. The whirling flame heats the crucible uniformly and when the furnace is operated with excess gas supply, a reducing atmosphere is maintained within the crucible.

The furnace proper consists of three easily replaceable fire-clay parts, namely, a lower cylinder containing the three tangential

<sup>a</sup> Ricketts, E. B., Discussion of paper by L. Marks, The clinkering of coal: Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 801-833.

tuyères, and forming the bottom of the furnace, a removable upper cylinder 7 inches in internal diameter and 7 inches high, and a cover plate  $1\frac{1}{2}$  inches thick, having a vent hole in the center for the flue gas.

The manufacturers were asked to modify the stock design by furnishing the upper cylinder with two holes in the side—a 2-inch observation hole with its center 4 inches from the top of the cylinder (excluding cover plate), and a  $\frac{3}{4}$ -inch thermocouple hole 90° to the right of the observation hole; the bottoms of these two holes are in the same horizontal plane. The interior of the furnace is cylindrical and approximately 7 inches in diameter and 11 inches high. A counterbalanced sheet-iron canopy 24 inches in diameter was connected with a telescopic 8-

inch flue to an exhaust system to conduct the hot gases out of the room. The canopy is shown in a raised position in Plate IV, *B*; when in use it is pulled down to the furnace cover.

The joint between the upper and the lower cylinder was made fairly gas tight by spreading on the top of the lower cylinder a thick paste of alundum cement to a depth of one-half inch and then firmly pressing the upper cylinder into place. The outer part of the joint was also smoothed over with alundum cement.

The interior of the furnace as arranged for making a test is shown in figure 31. The ash cones *a* are supported on a plate of alundum cement serving as a cover for the crucible *b*, which is 4 inches high and 3 inches in diameter at the bottom, outside dimensions. The cone-supporting crucible is within the crucible *d*, which with the cover *c* serves as a muffle. Crucible *d* is 7 inches high, 5 inches in diameter at the top, and 3 inches in diameter at the bottom, and is provided with observation and thermocouple holes corresponding to those in the furnace cylinder. The platinum and platinum-rhodium thermoelement is protected from the furnace gases by a glazed Marquardt porcelain tube *e* one-fourth inch in diameter. A fused silica tube *f*,  $1\frac{1}{8}$  inches in external diameter and 6 inches

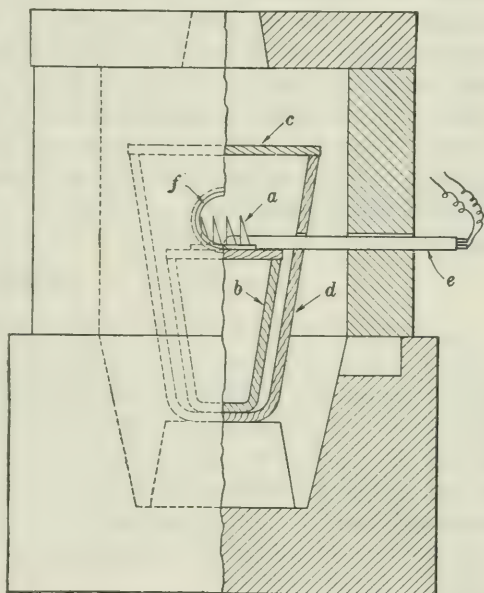


FIGURE 31.—Section of No. 3 melter's furnace arranged for fusion tests.

long, is placed in the 2-inch observation hole of the furnace, the inner end projecting through the wall of the crucible *d*, and the other end projecting out of the furnace a distance of 2 inches. A brass sleeve carrying a thin glass window was slipped on the outer end of the observation tube to prevent the escape of burning gas, which would have interfered with convenient observation of the cones.

The fire-clay furnace cylinders and cover will withstand a temperature of  $1,650^{\circ}$  C. It has, however, been difficult to obtain suitable refractory crucibles. Fused-silica ware was first used but was later abandoned on account of high first cost and short life owing to crystallization; alundum ware also went to pieces after a few runs. Finally the ordinary hard burned-clay assay crucibles were tried and found to be suitable, provided they were not heated to a temperature exceeding  $1,500^{\circ}$  C.

The average life of a crucible under these conditions is six runs; however, they cost only a few cents each, and are quickly replaced. Experiments are being made with various materials in order to obtain a cheap and durable material that may be used for temperatures up to  $1,650^{\circ}$  C.

#### METHOD OF OPERATION.

Natural gas, that used by the city of Pittsburgh, Pa., was supplied to the furnace at a pressure of approximately 10 to 12 inches water gage, through a  $\frac{3}{4}$ -inch pipe; air was supplied from a Root blower through a  $1\frac{1}{2}$ -inch pipe. The blower developed a pressure of 2 to 3 pounds to the square inch. As this pressure was inadequate for attaining temperatures above  $1,500^{\circ}$  C. an ordinary oxygen tank was connected to the air line and the air was enriched with oxygen whereby temperatures up to the melting point of platinum ( $1,755^{\circ}$  C.) were readily obtained.

With stronger air pressure, at least 5 pounds per square inch, temperatures up to  $1,700^{\circ}$  C. should be easily obtained without recourse to oxygen.

The coal ash was prepared and the cones were mounted in the manner described on pages 29–30.

Although several cones can be heated simultaneously in the gas furnace as shown in figure 31, all tests described in the following experiments were made with single cones, in order to eliminate any possible influence of volatile constituents of one cone on the softening point of another cone. The mounted cone having been placed in proper position in the crucible *d* (fig. 31) with the cover *c* in place, the gas was turned on, ignited, and allowed to burn about 10 minutes before the cover plate of the furnace was replaced; during this time



the air and gas was gradually increased so as to slowly heat the crucible without cracking it. After the cover plate was in place on the furnace, the proportion of air was increased sufficiently to cause the combustion to take place just above the tuyères, and yet maintain a flame at least 6 inches high above the opening in the cover plate. From this point the temperature was gradually increased by a suitable adjustment of gas and air until it was at least  $200^{\circ}$  C. below the probable down point of the cone; then a temperature increase of  $5^{\circ}$  C. per minute was started and maintained until deformation commenced. When the cone started to bend the rate of heat increase was reduced to  $2^{\circ}$  C. per minute, and this rate was maintained until the end of the test. During the entire period of heating a reducing atmosphere was maintained in the furnace by using the minimum amount of air necessary for attaining the desired temperatures. A luminous reducing flame issued from the opening of the cover plate to a height of at least 6 inches, except at the higher temperatures above  $1,450^{\circ}$  C., which could not be attained without a larger proportion of air to gas. Fortunately a strongly reducing atmosphere is not so essential at the higher temperatures, as refractory ashes, owing to their low content of iron oxide, are only slightly affected by oxidizing or reducing atmospheres.

#### COMPOSITION OF ATMOSPHERE SURROUNDING CONES.

While the furnace was operated under the conditions described above, samples of gas were taken from the interior of the muffle crucible *d* (fig. 31) at various temperatures between  $800^{\circ}$  and  $1,500^{\circ}$  C. The results of analyses of the gas samples, given in Table 19 following, show a fairly uniform composition over the given temperature range. Practically all the oxygen of the air had been consumed.

TABLE 19.—Results of analyses of gas samples taken at various temperatures from No. 3 melter's furnace.

Temperature where sample was taken.	Percentage by volume of—							Ratio.	
	CO <sub>2</sub> .	CO.	H <sub>2</sub> .	O <sub>2</sub> .	C <sub>2</sub> H <sub>4</sub> , etc.	CH <sub>4</sub> .	N <sub>2</sub> .	CO <sub>2</sub>	CO
	CO <sub>2</sub> + CO <sub>2</sub>	CO + CO <sub>2</sub>							
$^{\circ}$ C.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.	P. ct.
800.....	6.1	8.3	7.0	0.0	0.6	1.6	76.4	42	58
900.....	6.1	7.9	7.8	.5	.3	1.8	75.6	44	56
1,000.....	6.4	8.5	7.7	0	.2	.4	76.8	43	57
1,100.....	5.9	8.3	8.2	.3	.5	.5	76.3	42	58
1,200.....	6.2	8.5	9.1	.4	.2	.3	75.3	42	58
1,300.....	6.4	8.5	8.6	.1	.1	.3	76.0	43	57
1,400.....	6.9	7.3	6.5	.2	.2	.3	78.6	49	51
1,500.....	9.3	6.6	6.5	.2	.0	.3	77.1	59	41

These analyses do not show the real composition of the furnace atmosphere in that the water vapor was not determined. However,



it is possible to calculate the percentage of water vapor from the analysis of the natural gas used and the products of combustion, as follows:

CALCULATION OF PERCENTAGE OF WATER VAPOR IN GAS SAMPLE.

*Composition of natural gas used.*

Constituent.	Per cent.
Methane ( $\text{CH}_4$ )	78.7
Ethane ( $\text{C}_2\text{H}_6$ )	20.3
Nitrogen ( $\text{N}_2$ )	1.0
	100.0

78.7 c.c.  $\text{CH}_4$  forms on combustion 78.7 c.c.  $\text{CO} + \text{CO}_2$  and 157.4 c.c.  $\text{H}_2 + \text{H}_2\text{O}$ .

20.3 c.c.  $\text{C}_2\text{H}_6$  forms on combustion 40.6 c.c.  $\text{CO} + \text{CO}_2$  and 60.9 c.c.  $\text{H}_2 + \text{H}_2\text{O}$ .

119.3 218.3

Ratio of  $\text{H}_2 + \text{H}_2\text{O}$  to  $\text{CO} + \text{CO}_2$  in products of combustion =  $\frac{218.3}{119.3} = 1.83$

Hence water vapor in products of combustion =  $(\text{CO} + \text{CO}_2) 1.83 - \text{H}_2$ .<sup>a</sup>

The percentage of water vapor was calculated in this way for each analysis, and the results were combined with the results of the analysis in order to obtain the actual composition of the furnace atmosphere at various temperatures. The values so found are given in Table 20 following.

TABLE 20.—*Composition of furnace atmosphere at various temperatures.*

Temperature.  ° C.	Percentage by volume of—								Reducing gases. <sup>a</sup>	Oxidizing gases. <sup>b</sup>	Ratio of reducing gases to oxidizing gases.
	$\text{N}_2$ .	$\text{C}_2\text{H}_4$ .	$\text{CH}_4$ .	$\text{H}_2$ .	$\text{CO}$ .	$\text{CO}_2$ .	$\text{H}_2\text{O}$ .	$\text{O}_2$ .			
800.....	64.0	0.5	1.3	5.9	6.9	5.1	16.1	0.0	14.6	21.2	41:59
900.....	64.3	.3	1.4	6.6	6.7	5.2	15.1	.4	14.0	20.7	40:60
1,000.....	64.1	.2	.4	6.4	7.1	5.4	16.4	.0	14.1	21.8	39:61
1,100.....	64.8	.4	.4	7.0	7.0	5.0	15.1	.3	15.2	20.4	42:58
1,200.....	63.9	.2	.3	7.7	7.2	5.3	15.1	.3	15.4	20.7	43:57
1,300.....	63.9	.1	.3	7.3	7.2	5.4	15.7	.1	14.9	21.2	41:59
1,400.....	65.8	.2	.2	5.4	6.1	5.8	16.3	.2	11.9	22.3	35:65
1,500.....	62.9	.0	.3	5.3	5.3	7.6	18.4	.2	10.9	26.2	29:71

<sup>a</sup>  $\text{C}_2\text{H}_4 + \text{CH}_4 + \text{H}_2 + \text{CO}$ .

<sup>b</sup>  $\text{CO}_2 + \text{H}_2\text{O} + \text{O}_2$ .

Methane ( $\text{CH}_4$ ), ethane ( $\text{C}_2\text{H}_4$ ), hydrogen ( $\text{H}_2$ ), and carbon monoxide ( $\text{CO}$ ) are reducing gases; oxygen ( $\text{O}_2$ ), carbon dioxide ( $\text{CO}_2$ ), and water vapor ( $\text{H}_2\text{O}$ ) are oxidizing gases; nitrogen may be regarded as a neutral gas having neither oxidizing nor reducing properties. On this basis the ratio of reducing to oxidizing gases was fairly constant at 40 to 60 in the temperature range between 800° and 1,300° C.; above 1,300° C. the atmosphere became more

<sup>a</sup> Neglecting water vapor in gas and air supplied to the furnace and assuming no other forms of carbon in combustion products.

oxidizing, the ratio being 29 to 71 at  $1,500^{\circ}$  C. There is seemingly no danger of obtaining in the gas furnace an atmosphere that is too reducing in character. However, care must be observed to maintain the largest possible excess of gas over air; otherwise the minimum softening point corresponding to a ferrous iron slag will not be obtained.

#### TESTING FOR MAGNETIC SLAG AND METALLIC IRON.

In connection with the fusion tests made in atmospheres of equal parts of hydrogen and water vapor and of equal parts of carbon dioxide and carbon monoxide, it was shown that ash cones fused in such atmospheres showed little or no magnetism when suspended in the field of a strong electromagnet. This test was therefore used for determining the efficiency of reduction in the gas furnace. The electromagnet (fig. 32) consisted of a rod of Swedish iron, *a*,  $6\frac{3}{4}$  inches long and 1 inch in diameter, upon which were wound 250 feet of No. 18 B. & S. gage insulated copper annunciator wire, *b*, in 10 layers, the whole being covered with electrician's tape to keep the wire in place. The fused cone was placed in the copper stirrup, *c*, which was free to swing on a thread supported from above. A current of  $3\frac{1}{2}$  amperes was used to energize the magnet.

A dilute solution of copper sulphate was poured over a freshly ground surface of a fused cone. Metallic iron was then easily detected when this surface was examined under the microscope, as any particles of iron became copper plated.

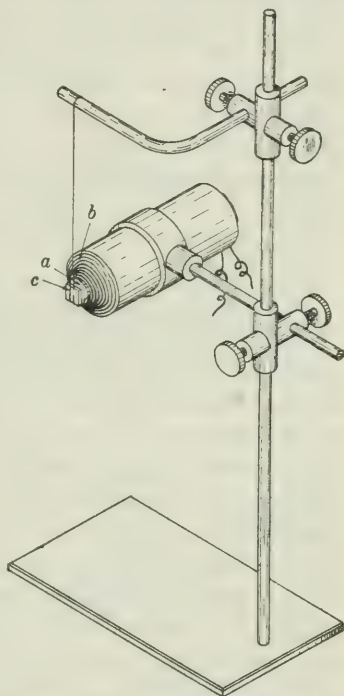


FIGURE 32.—Electromagnet used to determine magnetic properties of fused cones.

#### TEMPERATURE MEASUREMENTS.

Most of the temperature measurements were made with a thermoelement of platinum and platinum-rhodium and a Siemens and Halske high-resistance millivoltmeter. The cold junction was kept at the temperature of melting ice. The thermoelement was protected from the furnace gases by a glazed Marquardt porcelain tube of

five-sixteenth inch external diameter. This outfit could be safely used up to temperatures of  $1,550^{\circ}\text{C}$ . For higher temperatures an optical pyrometer of the Holborn-Kurlbaum type was used. The accuracy of both the thermocouple and the optical pyrometer was checked at regular intervals by determining the melting points of gold ( $1,063^{\circ}\text{C}$ .), diopside ( $1,391^{\circ}\text{C}$ .), and nickel ( $1,450^{\circ}\text{C}$ .), as in the earlier experiments.

The whirling flame produced by the three tangential burners heated the muffle crucible so evenly that it was difficult to see the cones and observe their deformation until means was provided for locally cooling the cones slightly below the temperature of the crucible wall. For this purpose a  $\frac{1}{4}$ -inch Marquardt porcelain tube was inserted through the openings provided for the thermocouple tube: the tube was so placed that when it was connected with the compressed-air pipe a jet of air was directed against the cones, cooling them momentarily, and thus rendering them visible.

#### RESULTS OF TESTS.

To furnish a basis for comparison of the results obtainable in the No. 3 melter's furnace with the results of fusion tests with other equipment, determinations were made of the softening temperatures of the same 48 coal ashes that had previously been fused in air, in an atmosphere of equal parts of hydrogen and water vapor, and in an atmosphere of equal parts of carbon monoxide and carbon dioxide. The size of cone and rate of heating was exactly the same in each of the different atmospheres. The results obtained are given in Table 13 (p. 68) and in figures 24 and 25 (pp. 70 and 71). It will be seen that most of the gas-furnace results agree fairly well with those obtained in the  $\text{CO-CO}_2$  atmosphere, the average difference for the two series being only  $10^{\circ}\text{C}$ ., and the average softening point curve *d* (fig. 24) for the gas furnace almost coinciding with the  $\text{CO-CO}_2$  curve *c*. There is, however, a difference, varying from  $30^{\circ}$  to  $70^{\circ}\text{C}$ ., between the average softening point curve *d* and the average softening point curve *b*, representing the results obtained in the atmosphere of hydrogen and water vapor, which produced the lowest softening temperatures.

#### COMPARISON OF RESULTS OBTAINED IN TWO DIFFERENT TYPES OF GAS FURNACES OPERATED UNDER MAXIMUM REDUCING CONDITIONS.

The experiments described showed that it was possible to obtain duplicate results in softening-temperature determinations made under maximum reducing conditions in the No. 3 melter's furnace.

The next step in investigating the suitability of the gas furnace for use in a standard method was to determine whether comparable results would be obtained in different types of gas furnaces, provided the furnace construction was such as to allow free access of the combustion gases to the ash cones.

As a different type of furnace, a No. 29 Meker muffle furnace was modified as shown in figure 33 by removing the muffle and replacing it with a porous alundum tube, *a*, 1¼ inches in internal diameter, the open front of the furnace around the alundum tube was closed with refractory fire clay, *b*; a thin rectangular plate *c*, 1½ by 3 inches, composed of kaolin and alumina mixed in equal proportions, was placed over the burner and directly under the alundum tube *a*, to spread the flame and cause uniformly distributed heating.

Within the tube *a* were placed two short alundum capsules *d* and *e*, the former with its closed end in front, near which was placed the cone *f*, mounted as usual in a base of kaolin and alumina. Radiation was cut down by placing the capsule *e* in front of the cone; a small opening in the closed end of this capsule permitted observation and measurement of the temperature with an optical pyrometer of the Holborn-Kurlbaum type. The temperature measurements were

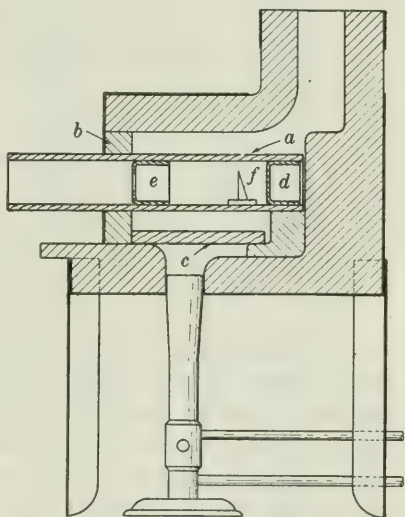


FIGURE 33.—Modified No. 29 Meker furnace.

checked in the usual manner by observing the melting points of pure gold wire and crystals of diopside. The burner connections were so arranged that either natural gas or coal gas could be used, with air at a pressure of 2 pounds per square inch. Owing to the low air pressure it was necessary to enrich the air with oxygen in order to attain the highest temperatures.

The method of making and mounting the ash cone, its size, and the rate of heating it were the same as in the tests with the No. 3 gas furnace. The furnace was operated at all times under maximum reducing conditions, a flame issuing from the chimney to a height of approximately 6 inches. Table 21 following shows the results of these tests in comparison with those with the No. 3 melter's furnace.



TABLE 21.—*Results of tests to determine softening temperatures in No. 3 melter's furnace and in modified Meker furnace.*

Ash sample No.	Softening temperatures in—			Differences.	
	No. 3 furnace with natural gas.	Meker furnace with natural gas.	Meker furnace with artificial gas.	2 and 3.	3 and 4.
1	2	3	4	5	6
	° C.	° C.	° C.	° C.	° C.
86. ....	1,076	1,087	1,074	-11	+13
88. ....	1,125	1,134	1,124	- 9	+10
83. ....	1,145	1,156	1,115	-11	+41
11. ....	1,156	1,165	1,137	- 9	+28
69. ....	1,166	1,179	1,177	-13	+ 2
100. ....	1,172	1,153	1,153	+19	0
90. ....	1,177	1,185	1,184	- 8	+ 1
93. ....	1,198	1,195	1,146	+ 3	+49
17. ....	1,218	1,212	1,189	+ 6	+23
68. ....	1,229	1,234	1,224	- 5	+10
97. ....	1,236	1,266	1,276	-30	-10
76. ....	1,250	1,248	1,219	+ 2	+29
13. ....	1,262	1,288	1,329	-26	-41
18. ....	1,277	1,271	1,224	+ 6	+47
72. ....	1,304	1,318	1,316	-14	+ 2
67. ....	1,316	1,329	1,304	-13	+25
74. ....	1,327	1,295	1,295	+32	0
95. ....	1,325	1,283	1,291	+42	- 8
89. ....	1,325	1,295	1,288	+30	+ 7
91. ....	1,341	1,283	1,318	+58	-35
77. ....	1,401	1,358	1,358	+43	0
Average. ....				+ 4½	+ 9

A representative lot of 21 coal ashes, varying in softening temperatures from 1,070° to 1,400° C., were tested in the two furnaces, the determinations in the No. 3 melter's furnace being made by one of the authors,<sup>a</sup> and the determinations in the Meker furnace being made by another member<sup>b</sup> of the laboratory force. Thus the use of a reducing atmosphere in a gas furnace was put to a more severe test by having different operators as well as different types of furnaces and pyrometers. The agreement in the results obtained, as shown in Table 21 and in figure 34 is even better than was expected and is within the requirements of a standard method. The largest difference was 45° C., whereas 75 per cent of the samples checked within 25° C. The average difference for the series was 4½° C.

#### COMPARISON OF RESULTS OBTAINED WITH NATURAL AND WITH ARTIFICIAL GAS.

The tests described were all made with natural gas as the furnace fuel. The results of tests with artificial gas shown in the table and in figure 34 are explained later. The combustible constituents of the

<sup>a</sup> A. E. Hall, assistant chemist.<sup>b</sup> H. A. Depew, junior physical chemist.

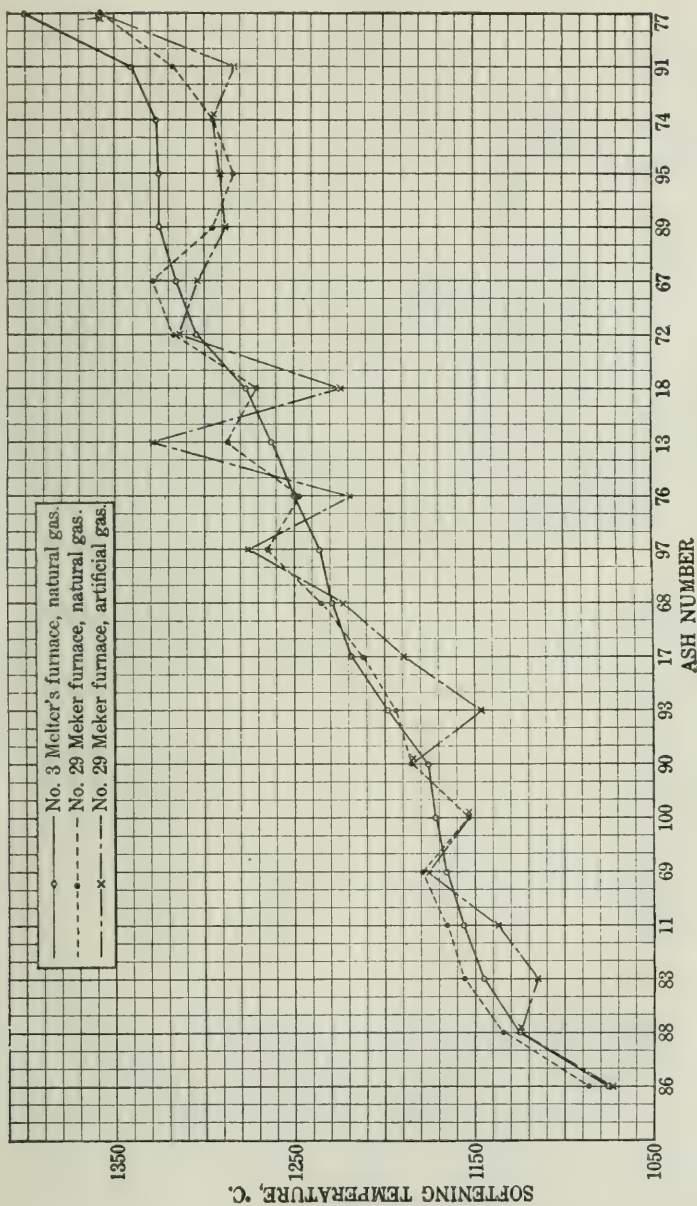


FIGURE 34.—Curves showing softening temperatures determined in No. 3 gas furnace and in modified No. 29, Meker furnace.

natural gas used in the city of Pittsburgh, Pa., comprise paraffin hydrocarbons only, the composition being as follows:<sup>a</sup>

*Analysis of natural gas used at Pittsburgh, Pa.*

Constituent.	Per cent.
Nitrogen ( $N_2$ )	1.6
Methane ( $CH_4$ )	84.7
Ethane ( $C_2H_6$ )	9.4
Propane ( $C_3H_8$ )	3.0
Butane ( $C_4H_{10}$ )	1.3
	100.0

In order to determine whether the composition of the fuel gas used had any influence on the softening temperature of an ash when heated under reducing conditions, the softening points of the same lot of ash samples were again determined in the Meker furnace under exactly the same conditions as before except that artificial gas was used instead of natural gas. The artificial gas used in Pittsburgh is made up of approximately 1 part of carburetted water gas and 3 parts of coal gas. Burrell, Seibert, and Robertson<sup>b</sup> give the following complete analysis for this gas:

*Analysis of Pittsburgh artificial gas.*

Constituent.	Formula.	Per cent.
Carbon dioxide	( $CO_2$ )	2.63
Oxygen	( $O_2$ )	.81
Carbon monoxide	( $CO$ )	13.25
Hydrogen	( $H_2$ )	37.33
Methane	( $CH_4$ )	31.13
Ethane	( $C_2H_6$ )	2.10
Propane	( $C_3H_8$ )	.43
Ethylene	( $C_2H_4$ )	6.05
Propylene	( $C_3H_6$ )	.60
Butylene	( $C_4H_8$ )	.11
Benzene	( $C_6H_6$ )	1.33
Nitrogen	( $N_2$ )	4.23
		100.00

The results obtained with the artificial gas have been given in Table 21 and in figure 34. The determinations in artificial gas averaged 10° C. lower than those in natural gas. The largest deviation was 49° C., and only 5 samples in a total of 21 deviated more than 30° C. These differences are little greater than would be expected in a

<sup>a</sup> Burrell, G. A., Seibert, F. M., and Robertson, I. W., Analysis of natural gas and illuminating gas by fractional distillation at low temperatures and pressures: Tech. Paper 104, Bureau of Mines, 1915, p. 16.

<sup>b</sup> Same work, p. 16 and p. 28.

parallel series of softening temperature determinations in which the same gas was used; hence the use of natural gas in one laboratory and artificial gas in another should not interpose any obstacle in the way of obtaining closely similar results.

#### IGNITION OF ASH IN OXYGEN.

The effect of unburned carbon in the ash in causing puffing or intumescence of the melting ash has been discussed, especially with reference to softening tests made in an atmosphere of hydrogen and water vapor. In the  $H_2$ - $H_2O$  atmosphere many of the cones had a marked tendency to swell even when the ash had been repeatedly ground and reignited in air and was finally made up into cones without the use of any carbonaceous binding material. Experiments made with the addition of small amounts of sugar carbon or dextrin did not produce any appreciable difference in the softening temperature or swelling tendencies of the ash; hence it was concluded that under the slow rates of temperature increase ( $2^\circ$  C. per minute) used, the carbonaceous material reacted with the atmosphere and was removed from the system before the ash began to soften, and that the swelling in  $H_2$ - $H_2O$  atmospheres was due to causes other than the presence of carbon.

In  $CO$ - $CO_2$  atmospheres and in the reducing atmosphere of the gas furnace, swelling of the cones was comparatively infrequent. However, a particularly troublesome ash in this respect led to igniting the ash in a current of pure oxygen for several hours at a temperature of  $850^\circ$  C. This treatment practically eliminated swelling of the cone in the reducing atmosphere of the gas furnace, and greatly reduced the degree of swelling when the ash was fused in the  $H_2$ - $H_2O$  atmosphere. As swelling of the cone makes the softening point less distinct, and practically prevents the determination of the fluid temperature, it was deemed advisable to regrind the ashes and subject them to a second ignition in oxygen for a period of two hours, at a temperature of  $800^\circ$  to  $850^\circ$  C.

This ignition was conveniently made in the improvised electric furnace shown in figure 35. It consisted of a fused-silica tube *a*,  $2\frac{3}{4}$  inches in internal diameter and 18 inches long, and having a wall one-fourth inch thick. It was open at one end and drawn down at the other end to a tube *b*, of three-eighths inch external diameter. On this tub was wound 90 feet of nichrome ribbon *c*, one-eighth inch wide and 0.032 inch thick (No. 20 B. & S. gage), the turns being as close as possible without touching; the winding was covered with a coating of alundum cement. The silica tube was supported at each end by asbestos (transite) board three-fourths inch thick, which was cut to fit snugly into the sheet-iron shell of the furnace. The space



between the silica tube and the shell was packed with kieselguhr (infusorial earth). The sheet-iron cylindrical jacket was 10 inches in diameter and  $17\frac{1}{2}$  inches long. Oxygen was supplied from a tank through a rubber tube and a bubbling bottle at the rate of 3 to 5 bubbles per second, the rubber tube being connected to the silica tube at *b*.

Before the ash was ignited it was ground for 20 or 30 minutes in a mechanical agate mortar grinder, which reduced the ash to 200 mesh and finer. Five to ten grams of this finely ground ash was placed in a silica or porcelain capsule *d*  $1\frac{3}{4}$  inches in diameter and five-eighths inch deep, and was transferred to the furnace. Six of these could be placed in the furnace at one time. The open end of the furnace was closed with a snugly fitting plug of "transite." The thermocouple was inserted through a hole in this plug. After one

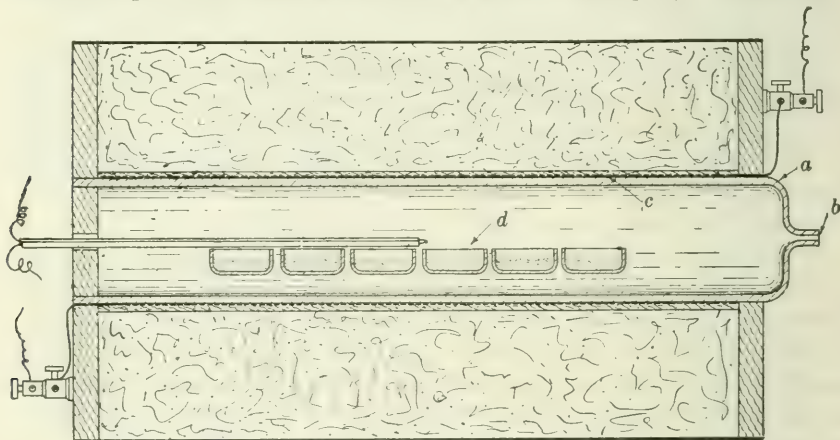


FIGURE 35.—Electric furnace for igniting ash in atmosphere of oxygen.

or two runs with the thermocouple, the temperature could be estimated with sufficient accuracy by the eye.

In heating this furnace from room temperature to  $800^{\circ}\text{C.}$ , a current of 5 amperes was used during the first 10 minutes: and then 10 amperes until  $800^{\circ}\text{C.}$  was reached, 30 to 40 minutes being required in all. Five to six amperes was required to maintain the temperature at  $800^{\circ}\text{C.}$  The maximum voltage was 110 volts.

This method of ignition was used in all subsequent experiments.

#### INFLUENCE OF SIZE AND SHAPE OF CONE.

The ordinary Seger cone used in the ceramic industries is so proportioned that on softening it describes a smooth bend or half circle, the tip touching the base. In the early part of this investigation it was found that similar cones made of molded coal ash did not, as a rule, bend as uniformly as the standard Seger cones. Certain ashes

had a decided tendency to flow down into a somewhat spherical lump without bending. Inclination of the cone did not solve the difficulty but, on the contrary, introduced more variation in the results, owing to shrinking and warping of the cone as the sintering temperature was approached. The most uniform results appeared to be obtained with a rather slender cone placed in a vertical position. A cone 1 inch high, having an equilateral triangular base, each side of which was three-sixteenths inch long, was adopted as a tentative standard and used in most of the tests previously described.

On extending this investigation to a wide variety of coal ashes some objections to the slender form of cone became evident, in that the softening-temperature determinations of certain types of ashes could not be duplicated within the usual limits ( $30^{\circ}$  C.). These differences were due to irregularities in the manner of deformation. Some cones flowed or "slumped" down into a lump without bending; other cones bent over in the usual manner. The down point of such cones was always lower, sometimes as much as  $200^{\circ}$  C. Previously described experiments (pp. 79-86) have shown the impossibility of making the cones composed of certain types of ashes describe a smooth bend on softening even when the cones are mounted in a horizontal position. Furthermore, the deformation temperature of inclined or horizontally mounted cones represents in many instances a comparatively incomplete state of fusion. The authors believe that serious clinker trouble in a furnace corresponds to a more complete fusion of ash, a state in which the resulting slag flows from the force of the gravity alone, without the aid of a bending moment. Reasoning from this point of view it was decided to use a cone with a wider base in proportion to the altitude so that the vertically mounted cone would never bend but always flow or "slump" down into a spherical lump, the temperature at which the cone attained this condition to be taken as the "deformation point" or "softening temperature."

In order to determine the best proportions of base to altitude, 12 ashes, whose softening temperatures ranged from  $1,050^{\circ}$  to  $1,550^{\circ}$  C., were molded into cones of the following sizes:  $\frac{3}{16}$  by  $\frac{1}{2}$  inch,  $\frac{3}{16}$  by  $\frac{5}{8}$  inch,  $\frac{3}{16}$  by 1 inch, and  $\frac{1}{4}$  by  $\frac{3}{4}$  inch. These ashes were selected as far as possible from those that had previously given trouble in irregular deformation. The cones were prepared in the usual manner and one of each size was mounted on the same kind of refractory base, and was placed in the No. 3 gas furnace in the position shown in figure 31. An exploration of the interior of the muffle crucible with the thermocouple showed a maximum variation in temperature of only  $5^{\circ}$  C.; hence each of the four different sizes of cones of a given ash was subjected to the same heat treatment, and any variation of results must have been due only to differences in the size and shape of the cones. The furnace was operated with a maximum reducing

flame. From a temperature of 800° C. the rate of heat increase was 5° C. per minute until initial deformation of any cone was noticed; the rate of heat increase was then 2° C. per minute until the last cone had either bent with the tip touching the base, or, failing to bend, had collapsed into a spherical lump. The temperature at which each cone reached one or the other of these conditions was recorded as the softening temperature. All the determinations were made in duplicate in order to obtain some data on the tendency toward variation in the manner of deformation of the several different sizes of cones.

## RESULTS OF EXPERIMENTS.

In nearly all the tests the slender cone, 1 by  $\frac{3}{16}$  inch, described the usual Seger-cone bend, whereas practically each of the other cones settled down into a somewhat spherical lump without bending. The results of the duplicate determinations for each size of cone, which are given in Table 22 following, show that the slender cones, which bent in the tests, were more susceptible to variable results than the cones with wider bases, which softened to a lump, the average difference in results of duplicate tests of a cone  $\frac{3}{16}$  by 1 inch being 18.5° C., as compared to 6°, 6.5°, and 8° C., for the nonbending cones.

TABLE 22.—Results of tests to determine softening temperatures in No. 3 melter's furnace with 4 different sizes of cones.

[Results in centigrade degrees.]

Ash sample No.	No. 1 cones, 1 inch by $\frac{1}{8}$ inches.			No. 2 cones, $\frac{3}{4}$ by $\frac{1}{4}$ inch.			No. 3 cones, $\frac{5}{8}$ by $\frac{3}{16}$ inch.			No. 4 cones, $\frac{1}{2}$ by $\frac{3}{16}$ inch.			Difference, No. 1 cones and average for No. 2 and No. 3 cones.
	Softening temperature.	Average.	Difference.	Softening temperature.	Average.	Difference.	Softening temperature.	Average.	Difference.	Softening temperature.	Average.	Difference.	
88.....	$\left\{ \begin{array}{l} 1,111 \\ 1,124 \end{array} \right\}$	1,117	13	$\left\{ \begin{array}{l} 1,122 \\ 1,124 \end{array} \right\}$	1,123	2	$\left\{ \begin{array}{l} 1,124 \\ 1,124 \end{array} \right\}$	1,124	0	$\left\{ \begin{array}{l} 1,124 \\ 1,124 \end{array} \right\}$	1,124	0	— 7
104.....	$\left\{ \begin{array}{l} 1,062 \\ 1,072 \end{array} \right\}$	1,067	10	$\left\{ \begin{array}{l} 1,132 \\ 1,142 \end{array} \right\}$	1,137	10	$\left\{ \begin{array}{l} 1,132 \\ 1,132 \end{array} \right\}$	1,132	0	$\left\{ \begin{array}{l} 1,101 \\ 1,132 \end{array} \right\}$	1,116	31	— 68
105.....	$\left\{ \begin{array}{l} 1,190 \\ 1,195 \end{array} \right\}$	1,193	5	$\left\{ \begin{array}{l} 1,195 \\ 1,195 \end{array} \right\}$	1,195	0	$\left\{ \begin{array}{l} 1,195 \\ 1,195 \end{array} \right\}$	1,195	0	$\left\{ \begin{array}{l} 1,195 \\ 1,195 \end{array} \right\}$	1,195	0	— 2
108.....	$\left\{ \begin{array}{l} 1,163 \\ 1,169 \end{array} \right\}$	1,166	6	$\left\{ \begin{array}{l} 1,201 \\ 1,236 \end{array} \right\}$	1,218	35	$\left\{ \begin{array}{l} 1,211 \\ 1,236 \end{array} \right\}$	1,223	25	$\left\{ \begin{array}{l} 1,201 \\ 1,206 \end{array} \right\}$	1,204	5	— 55
107.....	$\left\{ \begin{array}{l} 1,236 \\ 1,257 \end{array} \right\}$	1,247	21	$\left\{ \begin{array}{l} 1,246 \\ 1,257 \end{array} \right\}$	1,252	11	$\left\{ \begin{array}{l} 1,246 \\ 1,257 \end{array} \right\}$	1,252	11	$\left\{ \begin{array}{l} 1,236 \\ 1,236 \end{array} \right\}$	1,236	0	— 5
80.....	$\left\{ \begin{array}{l} 1,153 \\ 1,201 \end{array} \right\}$	1,177	48	$\left\{ \begin{array}{l} 1,331 \\ 1,342 \end{array} \right\}$	1,337	11	$\left\{ \begin{array}{l} 1,331 \\ 1,342 \end{array} \right\}$	1,337	11	$\left\{ \begin{array}{l} 1,331 \\ 1,342 \end{array} \right\}$	1,337	11	—160
67.....	$\left\{ \begin{array}{l} 1,298 \\ 1,356 \end{array} \right\}$	1,327	58	$\left\{ \begin{array}{l} 1,353 \\ 1,361 \end{array} \right\}$	1,357	8	$\left\{ \begin{array}{l} 1,353 \\ 1,361 \end{array} \right\}$	1,357	8	$\left\{ \begin{array}{l} 1,353 \\ 1,356 \end{array} \right\}$	1,355	3	— 30
74.....	$\left\{ \begin{array}{l} 1,321 \\ 1,353 \end{array} \right\}$	1,337	32	$\left\{ \begin{array}{l} 1,353 \\ 1,364 \end{array} \right\}$	1,359	11	$\left\{ \begin{array}{l} 1,353 \\ 1,364 \end{array} \right\}$	1,359	11	$\left\{ \begin{array}{l} 1,353 \\ 1,364 \end{array} \right\}$	1,359	11	— 22
109.....	$\left\{ \begin{array}{l} 1,391 \\ 1,407 \end{array} \right\}$	1,399	16	$\left\{ \begin{array}{l} 1,407 \\ 1,407 \end{array} \right\}$	1,407	0	$\left\{ \begin{array}{l} 1,407 \\ 1,407 \end{array} \right\}$	1,407	0	$\left\{ \begin{array}{l} 1,407 \\ 1,407 \end{array} \right\}$	1,407	0	— 8
110.....	$\left\{ \begin{array}{l} 1,496 \\ 1,496 \end{array} \right\}$	1,496	0	$\left\{ \begin{array}{l} 1,505 \\ 1,507 \end{array} \right\}$	1,506	2	$\left\{ \begin{array}{l} 1,505 \\ 1,507 \end{array} \right\}$	1,506	2	$\left\{ \begin{array}{l} 1,496 \\ 1,507 \end{array} \right\}$	1,502	11	— 10
75.....	$\left\{ \begin{array}{l} 1,496 \\ 1,501 \end{array} \right\}$	1,499	5	$\left\{ \begin{array}{l} 1,507 \\ 1,512 \end{array} \right\}$	1,510	5	$\left\{ \begin{array}{l} 1,507 \\ 1,512 \end{array} \right\}$	1,510	5	$\left\{ \begin{array}{l} 1,507 \\ 1,512 \end{array} \right\}$	1,510	5	— 11
106.....	$\left\{ \begin{array}{l} 1,518 \\ 1,531 \end{array} \right\}$	1,525	13	$\left\{ \begin{array}{l} 1,531 \\ 1,531 \end{array} \right\}$	1,531	0	$\left\{ \begin{array}{l} 1,531 \\ 1,531 \end{array} \right\}$	1,531	0	$\left\{ \begin{array}{l} 1,531 \\ 1,531 \end{array} \right\}$	1,531	0	— 6
Average.....			19			8			6			6½	— 32



The effect of varying the size and the shape of the cones on the deformation points is clearly shown in figure 36, in which the average softening temperature of each ash and of cones of each different size is plotted. The results for the No. 2 and No. 3 cones, which had the same ratios of base to altitude, are always within 10 degrees of each other. The results for the No. 4 cone, the shortest tried, also agree fairly well with those for the No. 2 and No. 3 cones. All of these cones deformed to a lump without bending. On the other hand,

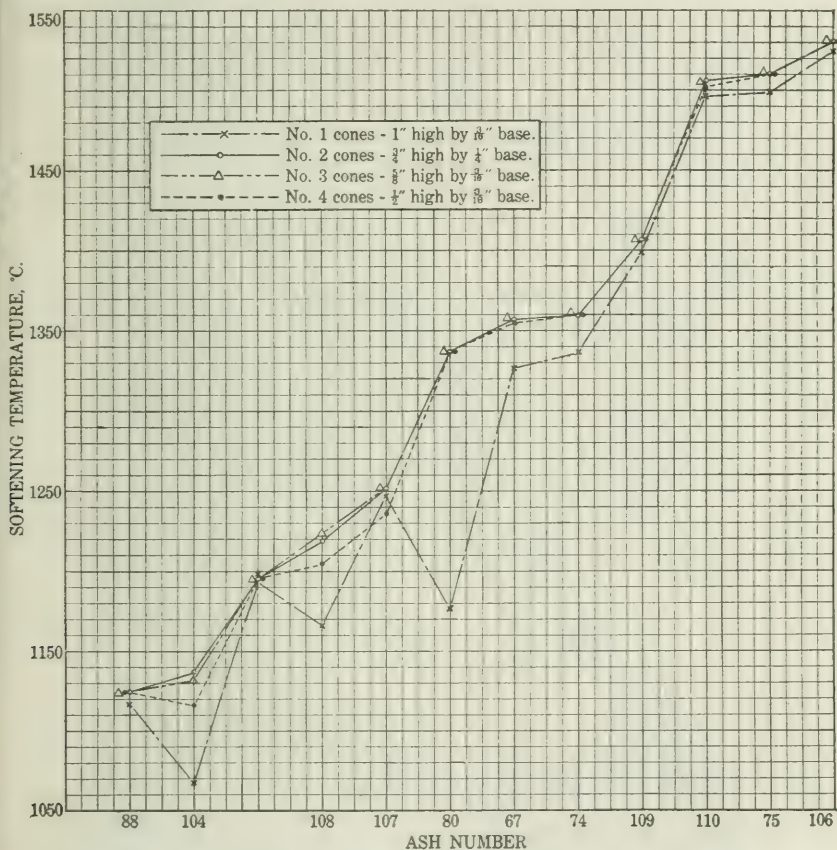


FIGURE 36.—Curves showing softening temperatures obtained in No. 3 melter's furnace with four different sizes of cones.

all of the No. 1 cones, the slender cones that usually bent on softening, had a lower softening point than the cones of the other three sizes, this difference ranging from 2° to 160° C. The observed softening point of a cone made from ash No. 80 may vary from 1,180° to 1,340° C., depending on whether the cone starts to bend at the incipient softening or whether it flows down to a lump without bending. As such variations are likely to occur with bending cones,



it seems best to rule out entirely this type of test piece and depend on one so proportioned that the force of gravity and surface tension will change the form from that of a pyramid or cone to that of an approximate sphere. Although perhaps the temperature at which this transition takes place can not be quite so definitely fixed as can the temperature at which the tip of a bending cone touches the base, the change is certainly less subject to large variations due to irregular

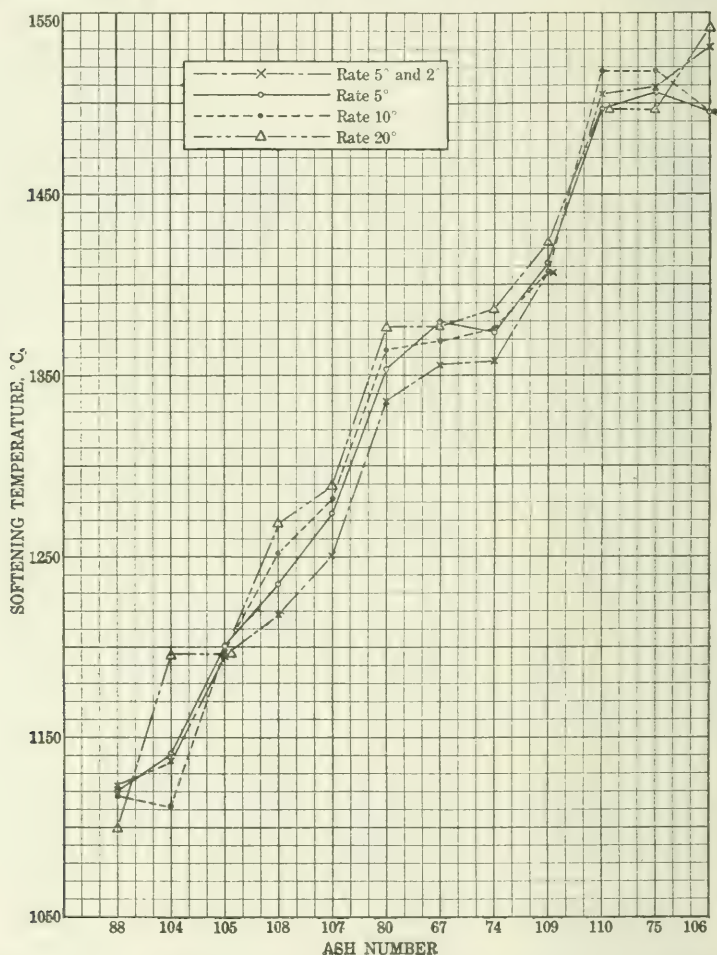


FIGURE 37.—Curves showing softening temperatures obtained in No. 3 melter's furnace at four different rates of heating.

bending, and in the opinion of the authors more nearly represents the state of fusion of ash when it forms troublesome clinkers.

As a result of the experiments described, a standard size of cone having an altitude of three-fourths inch, and a triangular base of one-fourth inch was used in the subsequent experiments. The

softening temperature was taken at the point where the cone deformed to a somewhat spherical lump, as shown in Nos. 2, 3, and 4 cones in Plate III, *B* (p. 66).

### INFLUENCE OF RATE OF HEATING.

Based on the results of experiments to determine the influence of rate of heating in oxidizing atmospheres of air and in reducing atmospheres of hydrogen, a temperature increase of  $5^{\circ}$  C. per minute to initial deformation, and then an increase of  $2^{\circ}$  C. per minute to final deformation was adopted as a standard rate in the experimental work so far described. In view of the importance of making the time of conducting a test as short as possible in commercial testing it seemed desirable to repeat these rate experiments under the new conditions prevailing in the gas furnace when operated under maximum reducing conditions.

The same 12 samples of coal ashes used in the "size-of-cone" experiments were molded into cones  $\frac{1}{4}$  by  $\frac{3}{4}$  inch and heated to the softening point in the No. 3 melter's furnace at four different rates, as follows:  $5^{\circ}$  C. per minute until initial softening, then  $2^{\circ}$  C. per minute,  $5^{\circ}$  C. per minute,  $10^{\circ}$  C. per minute, and  $20^{\circ}$  C. per minute. The results obtained are given in Table 23 and in figure 37. In general, the lowest rate of heating produced the lowest softening temperature. With only one exception the results of the  $5^{\circ}$  and  $10^{\circ}$  rates were within  $20^{\circ}$  of each other, and this exception deviated only  $30^{\circ}$ . It is therefore recommended that the rate of heating be kept between these limits. As a number of cones are usually heated simultaneously, it is advisable to start with a temperature of  $800^{\circ}$  C.

TABLE 23.—Results of tests to determine softening temperatures in No. 3 melter's furnace at four different rates of heating.

Ash sample No.	Rate of temperature increase per minute, $^{\circ}$ C.				Differences, $^{\circ}$ C.					
	5 and 2a.	5	10	20	5 and 2 and 5.	5 and 2 and 10.	5 and 2 and 20.	5 and 10.	5 and 20.	10 and 20.
88.....	1,123	1,120	1,118	$\left\{ \begin{array}{l} 1,072 \\ 1,127 \\ 1,099 \\ 1,189 \end{array} \right\}$	+ 3	+ 5	+24	+ 2	+21	+19
104.....	1,137	1,141	1,112	$\left\{ \begin{array}{l} 1,204 \\ 1,196 \end{array} \right\}$	- 4	+25	-59	+29	-55	-84
105.....	1,195	1,201	1,199	1,196	- 6	- 4	- 1	+ 2	+ 5	+ 3
108.....	1,218	1,235	1,252	1,268	-17	-34	-50	-17	-33	-16
107.....	1,251	1,273	1,282	1,289	-22	-31	-38	- 9	-16	- 7
80.....	1,336	1,353	1,364	1,377	-17	-28	-41	-11	-24	-13
67.....	1,357	1,379	1,369	1,377	-22	-12	-20	+10	+ 2	- 8
74.....	1,358	1,373	1,375	1,386	-15	-17	-28	+ 2	-13	-11
109.....	1,407	1,412	1,407	1,423	- 7	0	-16	+ 5	-11	-16
110.....	1,506	1,496	1,518	1,497	+10	-12	+ 9	-22	- 1	+21
75.....	1,509	1,507	1,518	1,497	+ 2	- 9	+12	-11	+10	+21
106.....	1,531	1,496	1,496	1,542	+35	+35	-11	0	-46	-46
Average.....					- 5	- 7	-18	- 2	-13½	-11½

$^{\circ}$  5° C. per minute until initial deformation of cone; then  $2^{\circ}$  C. per minute.

## DETERMINATION OF FLUID TEMPERATURE.

That the softening temperature of an ash, without any other information as to the change of viscosity of the mixture with temperature, must necessarily be a rather inadequate indication of prob-

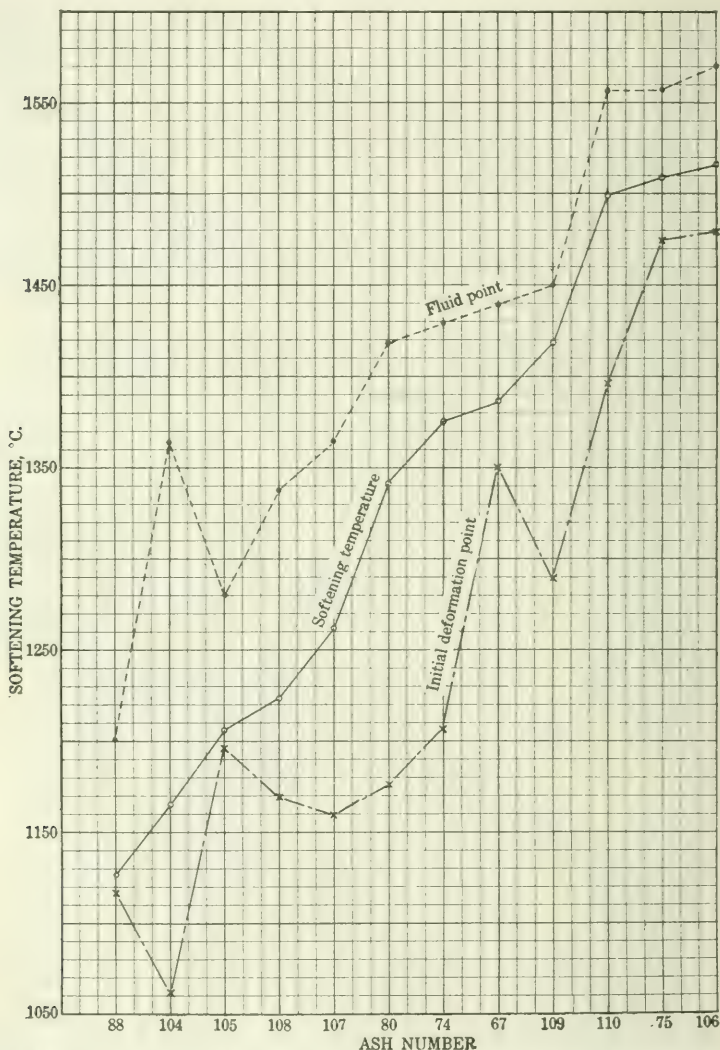


FIGURE 38.—Curves showing temperatures of initial deformation and softening and fluid temperatures of 12 ashes in No. 3 melter's furnace.

able clinkering properties has been generally recognized by most investigators who have studied this subject. Some ashes melt to a comparatively fluid slag in a short temperature range,  $10^{\circ}$  to  $20^{\circ}$  C.; others soften very slowly, there being an interval of  $50^{\circ}$  to  $150^{\circ}$  C.

between the initial deformation of the cone and its final softening point. This temperature range has been termed by the authors the "softening interval." It is believed that the length of the softening interval, when considered with the softening point, will ultimately be proved to have some connection to clinker formation. Furthermore, at the softening temperature the fusing ash is yet in a pasty and viscous condition; the fusion process has not reached the point where the slag is fluid enough to run and drip through the grate bars of a furnace, as sometimes happens in particularly troublesome clinker formation.

Therefore it is desirable by some simple method to determine the approximate fluid temperature of an ash. One method is to continue heating the cone, after the softening point is reached, to the temperature at which the spherical lump of slag becomes fluid and spreads out in a thin layer over the base in the manner of cone 5 in Plate III, *B* (p. 66). On trying this experiment with the same 12 samples of ashes used in the preceding experiments, it was found entirely practicable to determine this approximate fluid temperature. It was, of course, impossible to reproduce these fluid temperatures in duplicate tests as closely as the softening temperatures, as the end point was less definite than the point at which the cone became a spherical lump. The fluid point, however, was sufficiently defined to have some significance. For example, referring to figure 38, in which the results of these tests are plotted, ash sample 104 began to deform at  $1,060^{\circ}$  C., it reached the softening temperature at  $1,165^{\circ}$  C., and became fluid at  $1,365^{\circ}$  C.; the total temperature interval from initial deformation to fluid point was  $305^{\circ}$  C. On the other hand, ash sample 88, which began to deform at a higher temperature— $1,117^{\circ}$  C.—became fluid at a much lower temperature, namely,  $1,200^{\circ}$  C., the total temperature interval being only  $83^{\circ}$  C. This would appear to represent the type of ash that might cause troublesome clinkers; that is, the slag would probably spread out over the grate bars in the furnace at a comparatively low temperature, choking off the draft and interfering with combustion to a much greater degree than would ash sample 104. All the "critical points"—initial deformation point, softening temperature, and fluid point—should therefore be taken into consideration in judging the probable clinkering properties of an ash. These three points give approximate data on the change in viscosity with temperature, a change that varies greatly in different ashes. All the results obtained in this series of tests are given in Table 24 following.



TABLE 24.—*Results of tests to determine initial-deformation, softening, and fluid temperatures of 12 samples of ashes in No. 3 melter's furnace.*[Rate of temperature increase, 5° C. per minute; cones  $\frac{3}{8}$  by  $\frac{1}{8}$  inch; values in table in centigrade degrees.]

Ash sample No.	Critical points.			Fusion range.		
	Initial-deformation temperature.	Softening temperature.	Fluid temperature.	Start to down point, or softening interval.	Down point to fluid, or flowing interval.	Start to fluid, or total fusion interval.
88.....	1, 117	1, 127	1, 201	10	74	84
104.....	1, 062	1, 165	1, 364	103	199	302
105.....	1, 196	1, 206	1, 280	10	74	84
108.....	1, 169	1, 223	1, 337	54	114	168
107.....	1, 159	1, 262	1, 364	103	102	205
80.....	1, 176	1, 342	1, 418	166	76	242
74.....	1, 206	1, 375	1, 429	169	54	223
67.....	1, 350	1, 386	1, 439	36	53	89
109.....	1, 289	1, 418	1, 450	129	32	161
110.....	1, 396	1, 499	1, 557	103	58	161
75.....	1, 474	1, 509	1, 557	35	48	83
106.....	1, 479	1, 516	a 1, 570	37	54	91

a Estimated above 1,557° C.

#### DISCUSSION OF RESULTS OBTAINED IN GAS FURNACE WITH REDUCING ATMOSPHERE.

It was found possible to obtain consistent check results when the No. 3 melter's furnace and the modified Meker furnace were operated under maximum reducing conditions. Such conditions were obtained by allowing the combustion gases to circulate freely about the ash cones, and by so regulating the proportions of gas to air that a reducing flame at least 6 inches high burned at the outlet of the furnace. The softening temperatures thus obtained were generally between the values obtained in atmospheres of equal parts of  $H_2$  and  $H_2O$  and atmospheres of equal parts of  $CO$  and  $CO_2$ . Usually they were very close to the results obtained in the  $CO-CO_2$  atmospheres. Most of the iron oxide was reduced to the ferrous form, as shown by the nonmagnetic or only slightly magnetic nature of the fused cones. No metallic iron was found. A given ash sample showed practically the same softening temperature; whether natural or artificial gas was used in the furnace made no material difference. Analysis of the products of combustion from the interior of the furnace showed a ratio by volume of 40 per cent reducing to 60 per cent oxidizing gases, which is within the limits found necessary for a minimum softening temperature in  $CO-CO_2$  or  $H_2-H_2O$  mixtures, and also approximates the composition of the atmosphere that prevails in the fuel bed of a furnace, as shown by the work of Kreisinger, Ovitz, and Augustine.<sup>a</sup>

In view of these facts, the method of determining the fusibility of coal ash, in a gas furnace having a reducing atmosphere, may be

<sup>a</sup> Kreisinger, Henry, Ovitz, F. K., and Augustine, C. E., Combustion in the fuel bed of hand-fired furnaces: Tech. Paper 137, Bureau of Mines, 1916, p. 61.

accepted as answering the theoretical requirements of a standard method. A furnace of the type of the No. 3 melter's furnace used in the tests was found to possess the following practical advantages for use in commercial laboratories: (1) It is a standard type of furnace obtainable on the market at a low cost; (2) it is easily operated and repaired with the facilities available in the ordinary laboratory of a commercial plant; (3) owing to the tangential burners and swirling flame the required reducing atmosphere and a very uniform temperature can be maintained around the ash cones; (4) either a thermocouple or an optical pyrometer can be used (the thermocouple must, of course, be protected by a glazed Marquardt porcelain tube, and its use is limited to temperatures under  $1,550^{\circ}$  C.); (5) the fusibility of six different samples may be determined simultaneously, thus greatly decreasing the cost of a determination.

## RECOMMENDED PROCEDURE FOR STANDARD GAS-FURNACE METHOD.

### PREPARING THE ASH.

Fifty to one hundred grams of 60-mesh coal is spread out on a 6-inch fire-clay roasting dish, and completely converted to ash in a muffle furnace at a temperature of  $800^{\circ}$  to  $900^{\circ}$  C. Five to ten grams of this ash is transferred to an agate mortar<sup>a</sup> and ground to a fineness of 200 mesh. The ash is then placed in a silica or porcelain capsule, five-eighths of an inch deep and  $1\frac{1}{4}$  inches in diameter, and ignited for a period of two hours in a current of oxygen, at a temperature of  $800^{\circ}$  to  $850^{\circ}$  C. This ignition is made to insure complete and uniform oxidation of the ash.

### PREPARATION OF CONES.

The ignited ash is moistened with distilled water or 10 per cent dextrin solution and is worked into a plastic mass with a spatula or pestle. If the ash is finely ground a skilled operator can mold and mount cones without using any binding material; however, the authors were not able to detect any deleterious effect from using a 10 per cent solution of dextrin, provided the mounted cone was ignited at a red heat in an open muffle furnace before the fusion test was made. Cones made with dextrin solution are less fragile.

The plastic material is molded into small triangular pyramids three-fourths of an inch high and one-fourth of an inch wide at the side of the base. The pyramids are made by firmly pressing the plastic material with a steel spatula into a brass mold of the dimen-

<sup>a</sup> A mechanical agate-mortar grinder will save time where many determinations are made.

sions mentioned, the mold being similar to that shown in figure 7 (p. 29). The surface is then struck off smooth and the cone removed from the mold by applying a small knife blade at the base. By lubricating the mold at the start with a little vaseline the cone can be removed at once without waiting for it to dry. When the cones are dry they are mounted in a refractory base composed of equal parts of kaolin and alumina. The base mixture is moistened to make it workable, and a part of it is spread out on a sheet-iron plate. The cone is then mounted in a vertical position in a small hole made in the base, and base material is put into the hole around the bottom of the cone to fill the crevices and make the cone stand firmly. Usually five or six cones are mounted in one base in the manner shown in Plate III, *B* (p. 66). The sheet-iron plate with the test piece is then dried on a hot plate. If dextrin has been used as binder the cones are ignited at a red heat for 30 minutes in an open muffle furnace to remove the carbonaceous material.

#### METHOD OF HEATING.

The test piece is placed in the muffle crucible of the melter's furnace in the position shown in figure 31 (p. 91), the loosely fitting cover *c* is placed on the crucible, and the gas is ignited. It is necessary to allow the gas to burn about 10 minutes to heat the furnace parts before the large cover plate of the furnace is replaced; otherwise the flame is apt to blow out. During this time the flow of the gas and air is gradually increased at such a rate as will not cause the crucible to crack. After the cover plate is on the furnace, the volume of gas and air is increased sufficiently to cause the combustion to take place just above the tuyères and yet maintain a yellowish flame at least 6 inches above the opening in the cover plate. While such a flame is maintained above the furnace, the temperature is gradually increased, by a suitable adjustment of gas and air, to 800° C., when the rate of heat increase is slowed down to not less than 5° C. and not more than 10° C. per minute. This rate is maintained until the end of the test. It is also important that the 6-inch reducing flame be maintained at the furnace vent throughout the test, if possible, and at all events the temperature should be kept up to 1,450° C. After a test has been completed the supply of gas and air is turned off gradually to avoid cracking the muffle crucible. The critical points observed in the test are defined as follows:

(1) *The initial deformation temperature.*—The temperature at which the first rounding or bending of the apex of the cone takes place, as shown in cone 1 of Plate III, *B*. Such bending must not be confused with a shrinking or warping of the cone.



(2) *The softening temperature.*—The temperature at which the cone has fused down to a spherical lump as shown in cones 2 and 3 of Plate III, *B*. Cone 4 has almost reached the softening temperature.

(3) *The fluid temperature.*—The temperature at which the cone has spread out over the base in a flat layer, as represented by cone 5 in Plate III, *B*.

In order to avoid the confusion that might arise in an effort to report all of the critical points mentioned it is recommended that only the softening temperature be reported as such, the other two points being given in terms of temperature intervals above and below the softening temperature. For convenience these intervals are reported as follows:

(1) *The softening interval*, which is the difference between the softening temperature and the temperature of initial deformation.

(2) *The flowing interval*, which is the difference between the fluid temperature and the softening temperature.

Following is a specimen report in which these intervals are used:

*Ash No. 104.*

	° C.
Softening temperature .....	1,165
Softening interval .....	105
Flowing interval .....	200

Owing to the difficulty of obtaining on the market highly refractory muffle crucibles, commercial laboratories will probably not attempt to carry fusion tests above 1,500° C.; the great majority of coal ashes will soften below this temperature. Any ash that withstands 1,500° C. is in the refractory class and is acceptable as regards fusibility. Within these temperature limits the ordinary Denver fire-clay crucible No. K, 7½ inches high and 4⅝ inches in diameter at the top may be used. Crucibles should be ordered by the hundred, and the manufacturers should be required to drill two holes in the side of each, an observation hole 2 inches in diameter with its center 2 inches from the top of the crucible and a thermocouple hole three-fourths of an inch in diameter 90° to the right of the observation hole. The bottom of this hole should be in the same horizontal plane as the bottom of the observation hole.

A Denver fire-clay crucible No. E, 4½ inches high and 3 inches in diameter at the top, is suitable for supporting the ash cones in their proper position in the large crucible.

If the maximum temperature limit is placed at 1,500° or 1,650° C., a thermocouple made of platinum and platinum-rhodium, with a high-resistance millivoltmeter or a Northrup pyrovolver, is most convenient and accurate for measuring the temperature. The thermocouple must be protected from the furnace gases with a glazed Mar-



quardt porcelain tube. The outside diameter of this tube need not exceed five-sixteenths of an inch. The outfit should be checked frequently by mounting small pieces of pure gold or nickel wire or foil in place of the cones and observing their melting points in exactly the same manner as the melting points of the cones are observed. With a strong reducing atmosphere,  $1,450^{\circ}$  C. should be obtained for the melting point of the nickel and  $1,063^{\circ}$  C. for the gold. The thermocouple and the millivoltmeter should also from time to time be standardized throughout the temperature range for which they are used by a suitably equipped standardizing laboratory such as that of the United States Bureau of Standards.

If it should be desired to determine softening points above  $1,500^{\circ}$  C., special muffle crucibles of fused silica, magnesia, or corundite will be required, and the temperature measurements will of necessity be made with an optical pyrometer, preferably of the Holborn-Kurlbaum or Wanner type.

### SUMMARY AND CONCLUSIONS.

Attention is called to the empirical nature of the "fusing or softening-temperature" test and the necessity of adopting some standard and duplicatable method if it is to be used in specifications for the purchase of coal.

The influence of the more important factors affecting the softening temperatures of the coal ashes tested may be summarized as follows:

*Fineness of ash.*—Ash ground to an impalpable powder tended to soften at a slightly lower temperature than ash that would pass a 100-mesh screen. The difference averaged  $6^{\circ}$  C., and in no test exceeded  $40^{\circ}$  C. Ash pulverized to at least 200 mesh was preferred, as it could be molded into more substantial cones than 100-mesh material.

*Inclination of cones.*—Mounting the cones with a considerable inclination— $35^{\circ}$  or  $40^{\circ}$  from the vertical—caused premature deformation points in some cones, which bent only at or near the base at a comparatively early stage in the fusion process, before the ash had softened to the flowing point. Vertical or nearly vertical cones were more free from this source of variation. Horizontally mounted cones usually gave lower softening points than vertical cones, the difference varying from  $0^{\circ}$  to nearly  $200^{\circ}$  C. The average difference for 15 samples was  $49^{\circ}$  C. In general, horizontal or inclined cones indicated a softening point at too early a stage in the fusion process; hence vertically mounted cones are recommended.

*Size and shape of cone.*—The deformation of a cone depended to some degree on its size and shape. Within limits of  $\frac{1}{2}$  to  $2\frac{1}{2}$  inches high the actual size had little influence provided the shape was the same; that is, the ratio between the dimensions of the base and of

the altitude. Cones made of coal ash did not bend as uniformly as the standard pyrometric cones. Attempts to modify the ratio of base to altitude in order to obtain a more uniform deformation, like the usual Seger-cone bend, resulted in the selection of a rather slender type of cone—each side of base three-sixteenths of an inch; altitude, 1 inch—as having less tendency to soften to a lump without bending. However, later experience showed that certain ashes when molded into slender cones would bend when only a relatively small part of the ash mixture had fused, thus indicating a premature softening temperature; it was also impossible to prevent some ashes from fusing down to a lump even with the slender type of cone. It was, therefore, decided to eliminate entirely the bending tendency by increasing the width of the base; and to take as the softening temperature the point where the cone had softened and flowed down to a somewhat spherical lump. The optimum size for this purpose was determined experimentally and found to be a cone three-fourths of an inch high and one-fourth of an inch wide at the base. This end point was found reproducible within  $30^{\circ}$  C., and was practically free from the occasional large variations experienced with the slender bending cones.

*Carbonaceous matter in the ash.*—Tests in which all traces of carbon were removed and in which the cones were made up exclusively with distilled water, showed no appreciable difference in softening temperature when compared with similar tests in which the same ashes were made into cones with 10 per cent dextrin solution which was not burned out before the cones were inserted in the furnace. These tests were made in atmospheres of air, of hydrogen and water vapor, and of carbon monoxide and carbon dioxide at rates of heating not exceeding  $5^{\circ}$  C. per minute. However, in certain tests in the gas furnace with a reducing atmosphere, more rapid rates of heating caused swelling and intumescence, which was much less pronounced when the ash was previously ignited in oxygen for two hours. In routine work, ignition of the reground ash in oxygen promotes more definite and reliable softening points, especially when the original ash has been incompletely ignited.

*Rate of heating.*—In general, slower rates of heating gave lower softening points. Rates slower than  $2^{\circ}$  C. or faster than  $10^{\circ}$  C. per minute are not advisable. The effect of variations between these limits in purely oxidizing atmospheres was negligible. In a reducing atmosphere of hydrogen the lowest and most uniform results were obtained with a heat increase of  $2^{\circ}$  C. per minute; however, a temperature increase of  $5^{\circ}$  C. per minute until initial deformation of the cone occurred, and then reducing the rate to  $2^{\circ}$  C. per minute gave practically the same results and saved considerable time in making the test. In the gas furnace with reducing atmosphere, the optimum

rate of temperature increase was between  $5^{\circ}$  and  $10^{\circ}$  C. per minute. These limits are recommended for a standard rate of heating.

*Oxidizing or reducing atmosphere.*—The atmosphere in which the ash was heated proved by far the most important factor in causing large variations in the softening temperature. The highest softening points were obtained either in an atmosphere of air (platinum-wire resistance furnace), or in a strongly reducing atmosphere of carbon monoxide (Northrup furnace), which prevented the iron oxide from acting as a fluxing agent by reducing it to metallic iron before the softening of the ash began. The lowest softening temperatures were obtained in those atmospheres of mixed gases in which reduction of ferric oxide proceeded mainly to ferrous oxide, the most active phase in the reduction of iron ore as regards slag formation at lower temperatures. The maximum variation in softening temperatures due to different atmospheres ranged from  $134^{\circ}$  to  $396^{\circ}$  C.

*Fusibility of ash in various mixtures of hydrogen and water vapor.*—The softening temperatures of five different coal ashes were determined in various mixtures of hydrogen and water vapor, ranging from 100 per cent hydrogen to 100 per cent water vapor. These results, plotted in the form of curves, showed that for each of the ashes tested there was a high softening temperature in pure hydrogen on one end owing to reduction of iron oxide to metallic iron; a similar high softening temperature in water vapor or air on the other end owing to the iron oxide remaining for the most part in the form of ferric iron or magnetite; and a somewhat lower softening temperature in the middle part, in an atmosphere ranging from 30 to 70 per cent water vapor, owing to the reduction of most of the iron to the ferrous state, in which it combined to form fusible ferrous silicates.

*Fusibility of ash in various mixtures of carbon monoxide and carbon dioxide.*—Softening-temperature tests in various mixtures of carbon monoxide and carbon dioxide were also made with four of the ashes that had been tested in mixtures of hydrogen and water vapor. Softening-temperature curves similar to the curves obtained in tests with atmospheres of hydrogen and water vapor were obtained, each having a minimum region of fusion between approximate limits of 75 and 10 per cent carbon monoxide. However, it was found necessary to heat the ash cones more slowly in  $\text{CO-CO}_2$  atmospheres to attain approximately the same minimum point as was found in  $\text{H}_2\text{-H}_2\text{O}$  atmospheres at faster rates of heating. Even with a slower rate of heating in the former atmosphere the average difference in the minimum softening temperatures (down points) of a series of ashes tested in the two atmospheres was  $66.1^{\circ}$  C. The maximum difference was  $197^{\circ}$  C. The results obtained in  $\text{H}_2\text{-H}_2\text{O}$  atmospheres



were generally lower than in  $\text{CO-CO}_2$  atmospheres. The initial deformation points were practically the same in  $\text{CO-CO}_2$  and in  $\text{H}_2\text{-H}_2\text{O}$  atmospheres.

*Fusibility of ash in the reducing atmosphere of a gas furnace.*—It was found possible so to operate two types of gas furnaces, in which the combustion products had free access to the coal ash, that an atmosphere of approximately 60 per cent oxidizing and 40 per cent reducing gases was maintained around the coal ash. Softening temperatures similar to those previously obtained in mixtures containing equal parts of carbon monoxide and carbon dioxide were thus obtained in a much simpler type of furnace. By operating the gas furnace with the maximum excess of gas over air, the desired reduction of ferric to ferrous iron was obtained without the production of any metallic iron.

*State of oxidation of iron in ash cones fused in various atmospheres.*—Ash cones fused in oxidizing atmospheres of air, carbon dioxide, and water vapor contained 67 to 88 per cent of the total iron in the ferric form; in reducing atmospheres of hydrogen and carbon monoxide, 49 to 78 per cent of the iron was present as metallic iron. In mixtures containing equal parts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  or of  $\text{CO}$  and  $\text{CO}_2$  78 to 94 per cent of the iron was present as ferrous iron.

*State of oxidation of iron in clinker and slags.*—Analyses of clinker slags from two different boiler furnaces and one hand-fired experimental furnace showed that fuel-bed conditions are such as to favor the formation of clinkers containing iron principally in the ferrous state as was found in ash cones fused in mixtures of equal parts of  $\text{H}_2$  and  $\text{H}_2\text{O}$  or of  $\text{CO}$  and  $\text{CO}_2$ .

*Standard method of determining the softening temperature of coal ash.*—The method of determining the softening temperature of coal ash in a gas furnace with a reducing atmosphere is recommended as a standard method. The furnace is simple, it can be easily operated, and a number of tests can be made simultaneously. When the furnace is operated under the prescribed reducing conditions reproducible results can be obtained, approximating those of the more definite mixtures of equal proportions of  $\text{CO}$  and  $\text{CO}_2$ . A standard furnace design and procedure is recommended.

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14. FIELDNER, A. C., HALL, A. E., AND FEILD, A. L. The fusibility of coal ash. *Proc. Am. Soc. Testing Materials*, vol. 15, pt. 2, 1915, pp. 297-347. A general résumé of all investigations conducted by Bureau of Mines on the fusibility of coal ash.
15. HUBLEY, F. C. Clinkering properties of coal. *Proc. Eng. Club of Philadelphia*, vol. 32, January, 1915, pp. 35-85; reviewed in *Power*, vol. 40, 1914, p. 796; *Jour. Am. Soc. Mec. Eng.*, vol. 37, 1915, pp. 208-211; *Power*, vol. 44, 1916, pp. 523-25, 591-93. Describes the cone and the fusiometer methods of determining fusing temperature of coal ash. Latter method consists of making a cylinder of the ash one-half inch high by five-eighths inch in diameter under high pressure, placing it between

two carbon rods in gas furnace with  $1\frac{1}{2}$  pounds pressure on it, and heating until pointer attached to rod shows it to be half its original height. Hubley says softening range (temperature between first indication of softening and final point) is important; long range gives troublesome, gummy clinker, whereas short range gives porous, easily broken clinker. Specification of fusing temperature dependent on load conditions, etc.

16. KRESINGER, HENRY. Hand-firing soft coal under power-plant boilers. Tech Paper 80, Bureau of Mines, 1915, pp. 38-47. Clinker is fused ash; its formation is dependant on composition of ash and condition of fuel bed. Chief causes of clinkering are thick fuel bed, excessive stirring of fire, burning coal in ash pit, much slack in coal, closed ash-pit doors and preheating air admitted under grate. Precautions against clinkering are: carry thin fire, avoid excessive stirring, fire in small charges, keep burning coal from ash pit, keep ash-pit doors open, and, in very bad cases, use of limestone spread over grate. Gives instructions for burning coal containing much slack.
17. LE CHATELIER, HENRI. Étude sur la fusibilité des cendre des combustibles. Bull. Soc. D'Encourg. pour l'Ind. Nat., t. 102, 1902, pp. 223-229; abstracted in Jour. Soc. Chem. Ind., vol. 21. 1902, p. 459. Made fusing temperature tests by Seger-cone method. Found considerable variation in coals from same mine.
18. MARKS, L. S. Clinkering of coal; results of tests for effect of various constituents of the ash. Eng. News, vol. 64, 1910, p. 623. Added various ash-forming constituents of coal to a clinkering West Virginia coal and noted the effect on clinker formation. As remedy for clinkering advises reduction of combustion temperature or use of steam under grate.
19. ——— The clinkering of coal. Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 801-815; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, p. 206; Power, vol. 40, 1914, pp. 932-934. Gives as main factors influencing fusing temperature of ash: Character of atmosphere, size of cone, position of cone, situation of cone in furnace, and method of supporting cone. Advises horizontally mounted cone in oxidizing atmosphere. A general relation exists between fusing temperature and clinker trouble, but is not sufficiently definite to be of much practical use.
20. PALMENBERG, O. W. The clinkering of coal and its composition. The fusion temperature is not to be judged by the sulphur or iron content. Iron Age, vol. 93, 1914, pp. 410-411. Gives fusing temperatures of 38 coals with percentages of ash and sulphur in each, and percentage of  $\text{Fe}_2\text{O}_3$  in the ash of each. Palmenberg concludes that no relation is shown between the percentages of sulphur and iron and the fusing temperatures.
21. ——— Discussion of L. S. Marks's paper on "The clinkering of coal": Trans. Am. Soc. Mech. Eng., vol. 36, 1914, pp. 824-828; Jour. Am. Soc. Mech. Eng., vol. 37, 1915, pp. 211-212. Describes method of determining fusing temperature. Uses Meker gas furnace and optical pyrometer, and molds ash into a long slender cone.
22. ——— Fusion temperature of ash. Black Diamond, vol. 56, 1916, p. 403. Discusses effect of furnace atmosphere on the iron constituents of coal ash.
23. ——— The relation of composition of ash in coal to its fusing temperature. Jour. Ind. and Eng. Chem., vol. 6, 1914, pp. 277-279. See also No. 20.



24. PARR, S. W. Honeycomb and clinker formation. *Railway Rev.*, vol. 55, 1914, pp. 14-15. Paper read before convention of International Railway Fuel Association. Discusses nature of the chemical combinations in coals that have a tendency to produce honeycomb and clinker formations in locomotive boilers. In the absence of air, pyrite ( $\text{FeS}_2$ ) is decomposed by heat to ferrous sulphide, which is easily fusible and starts the formation of clinker and honeycomb. Clinker trouble can be minimized by eliminating "fines" especially where forced draft is used. A thin fire should be maintained with sufficient excess of air to burn  $\text{FeS}_2$  to  $\text{Fe}_2\text{O}_3$  without forming  $\text{FeS}$ .
25. PARSON, C. H. Steam for preventing clinker. *Power*, vol. 33, 1911, p. 240. Describes different kinds of clinker, notes losses incident to clinker troubles, and states that steam jet prevents clinker formations.
26. PHILLIPS, W. B. Further notes on coal impurities. *Coal Age*, vol. 2, 1912, pp. 111-112. Discusses papers of Bailey and Wadleigh on clinkering and fusibility of coal ash. Takes exception to their statements that there is no relation between the fusing temperature and the percentage of sulphur in the coal. Pyrite must be regarded as a source of clinker trouble.
27. PROST, EUGENE. Recherches sur les relations existant entre le degré de fusibilité et la composition des cendres de houille. *Rev. univ. des mines*, t. 31, 1895, pp. 87-98; *Moniteur sci.*, t. 46, 1895, pp. 560-565. See also English abstracts of his articles in *Coll. Guard.*, vol. 70, 1895, p. 796; vol. 74, 1897, p. 602; vol. 75, 1898, p. 473. Gives a number of ash analyses and relative fusibilities, and derives a formula for expressing the relative fusibility of ash from its composition. For further details see this bulletin, p. 2
28. QUICKEL, R. D. The clinkering of mixed coals. *Coll. Eng.*, vol. 34, 1914, pp. 368-371. Coals that do not form clinker when used alone may do so when mixed. Records experience with certain southern coals in locomotive practice. Describes two hard and molasses types of clinker. Gives tables of analyses and of silicate calculations.
29. RICKETTS, E. B. Discussion of L. S. Marks's paper, The clinkering of coal. *Trans. Am. Soc. Mech. Eng.*, vol. 36, 1914, pp. 830-833; *Jour. Am. Soc. Mech. Eng.*, vol. 37, 1915, p. 213. Gives determinations of fusing temperatures in gas furnace with Wanner pyrometer and horizontally mounted cones. Gives a curve, "Efficiency vs. ash-fusion temperature," derived from boiler tests. Considers fusing-temperature tests good indication of clinkering qualities.
30. STUCKENBERG, W. I. AND KOHOUT, J. F. Some points about fusion temperature of ash. *Black Diamond*, vol. 56, 1916, p. 234. Uses cone method and Seimatco pyrometer. Tests with raw and washed coals showed similar fusing temperatures, although the ash content and the sulphur content were lowered by washing. Authors assert that fusing temperature depends mostly on intrinsic ash and is not affected by extraneous impurities.
31. TUSPIN, S. U. The formation of clinker in coal. *Elec. World*, vol. 65, 1915, pp. 1184-1185. General discussion of reasons and remedies for clinkering.
32. VOIGHT, KARL. Ueber die Schmelzbarkeit der Aschen von Brennstoffen. *Ztschr. angew. Chem.*, Bd. 21, 1908, pp. 2461-2462. Claims that fusing-temperature test is of no practical value in buying coal.

33. WADLEIGH, F. R. Notes on the impurities in coal. *Coal Age*, vol. 1, 1912, pp. 1206-1209. A general article on the nature of clinker formation, kinds of clinker, and the determination of clinkering properties from the fusing temperature of the ash and from analyses of the ash.
34. WING, J. F. Management of water-gas generators. *Am. Gas Light Jour.*, vol. 92, 1910, pp. 730-732 and 772-776. Describes water-gas producer in which an extra grate is used and temperature is raised to make the clinker flow down upon the lower grate, whence it is easily removed.
35. EDITORIAL. The steam jet as a means of preventing clinkering in the boiler furnace. *Eng. News*, vol. 64, 1910, p. 632. Advises the use of steam jet as clinker preventive, and urges further study of the problem.

#### CONTRIBUTIONS TO THE PHYSICAL CHEMISTRY OF SLAG AND SILICATES.

36. AKERMANN, R. Ueber die zum Schmelzen verschiedener Hochofenschlacken erforderlich Wärmemenge. *Stahl u. Eisen*, Jahrg. 6, 1886, pp. 281-301, 387-396. Gives heat of formation, latent heat of fusion, and other physical data for various slags. One of the earliest works on the subject.
37. ALLEN, E. T., AND WHITE, W. P. Diopside and its relation to calcium and magnesium metasilicates. *Am. Jour. Sci.*, vol. 27, 1909, pp. 1-47. Describes results of using thermal method of determining melting-point curve of various mixtures of  $\text{CaSiO}_3$  and  $\text{MgSiO}_3$ . Describes eutectics, giving melting points. Only one stable form, identical with diopside was found; it had a melting point of  $1,380^\circ \text{C}$ .
38. ASHLEY, H. E. Slag constitution studied by means of the triaxial diagram with rectangular coördinates. *Trans. Am. Inst. Min. Eng.*, vol. 31, 1901, pp. 855-883. Discusses use of the triaxial diagram in plotting the data obtained by Hofmann on the formation temperatures of slags.
39. BABU, L. *Métallurgie générale*. Paris, 1904, vol. 1, pp. 470-543. Discusses general properties of slags, silicate degree, and formation and melting temperatures, and gives diagrams for two or more than two constituents.
40. BLEININGER, A. V. Some aspects of the physical chemistry of fusing silicates. *Trans. Am. Cer. Soc.*, vol. 9, 1907, pp. 419-460; *Sprechsaal*, Jahrg. 42, 1909, pp. 170-172. Enumerates various methods of attack upon ceramic physical-chemical problems and calls attention to some of the laws involved.
41. BLEININGER, A. V., AND BROWN, G. H. The behavior of fire bricks under load conditions at a temperature of  $1,300^\circ \text{C}$ . *Trans. Am. Cer. Soc.*, vol. 12, 1910, p. 337. Gives full description and results of test.
42. ——— The testing of clay refractories, with special reference to their load-carrying capacity at furnace temperatures. *Tech. Paper No. 7*, U. S. Bureau of Standards, 1911, 78 pp. Discusses composition and fusion of refractory clays, effect of heat on pure clays; effect of accessory constituents such as quartz, alumina, titanium oxide, iron oxide, alkalies, mica, lime, and magnesia upon the softening temperature of fire clays; effect of fluxes on the refractoriness; Richter's law; Bischof's refractory quotient; and effect of the RO in the Seger-cone series. Describes a granular-carbon resistance furnace used in determining the softening point of the fire clays.

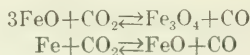
43. DAY, A. L., AND SHEPARD, E. S. The lime-silica system of minerals. *Am. Jour. Sci.* vol. 22, 1906, pp. 265-302. An exhaustive study of this binary system, by physico-chemical methods, thermal and microscopic. Calls attention to the fact that softening-temperature curves of mechanical mixtures molded in the form of cones do not give reliable data regarding melting points, as a cone, when heated, begins to weaken as soon as the eutectic begins to melt, and further progress is governed entirely by the relative quantity of eutectic present and its viscosity after melting. In general, the formation temperature is below the melting point of the fused mineral except where the constituents are coarsely ground and poorly mixed.
44. DOELTER y CISTERICH, C. A. *Handbuch der Mineralchemie*. Dresden, 1912, Bd. 1, pp. 628, 925-955. Discusses silicate formation, melting points, etc. Gives tables of melting points of common minerals, comparing points of different observers. Discusses various methods of determining melting point, temperatures, viscosity, and crystal formation. Describes metallurgical slags and their viscosity, crystallization of the slag minerals, etc.
45. ——— Die Schmelzen des metakalzium-silikates,  $\text{CaSiO}_3$  und des Alumo-silikates,  $\text{Ca}_3\text{Al}_2\text{Si}_2\text{O}_{10}$ . *Tonind. Ztg.*, Bd. 35, 1911, p. 118. Discusses measured electrical resistances.
46. ENDELL, K., AND RIEKE, R. Ueber die Umwandlungen des Kieselsäureanhydrid bei höheren Temperaturen. *Ztschr. anorg. Chem.*, Bd. 79, 1912, pp. 239-259. Describes experiments to determine melting and transformation points of various silica minerals in iridium furnace, with Ir-Ir Ru thermocouple.
47. FEILD, A. L. A method for measuring the viscosity of blast-furnace slag at high temperatures. *Tech. Paper 157*, Bureau of Mines, 1916, 27 pages. In the method described, the liquid slag is confined between two concentric cylinders of graphite. The outer is rotated and the inner is suspended and the torque exerted upon it is measured. The average viscosity at  $1,500^\circ \text{C}$ . of 8 slags measured was 301 ( $\text{H}_2\text{O}$  at  $20^\circ \text{C}$ . = 1), which is less than that of castor oil at room temperature but greater than that of olive oil. Apparatus could be used with temperatures up to  $1,600^\circ \text{C}$ ., but was not feasible with iron-bearing slags on account of graphite parts and reducing atmosphere.
48. FENNER, C. N. The stability relations of the silica minerals. *Am. Jour. Sci.* vol. 36, 1913, pp. 331-384. A study of the inversion temperatures of quartz, tridymite, and cristobalite. Gives melting point of cristobalite as  $1,625^\circ \text{C}$ .
49. FULTON, C. H. Principles of metallurgy. 1910. pp. 146-196, 245-288, 290-293. Discusses measurement of high temperatures, and gives composition, formation, and melting temperature of various silicate slags, with tables and curves. Outlines physical properties such as viscosity, specific heat, heat of formation, and latent heat of fusion, and discusses the system of Fe-FeS.
50. GREINER, F. E. Ueber die Abhängigkeit der Viscosität in Silikat-schmelzen von ihrer chemischen Zusammensetzung. *Inaug. dissertation*, Univ. Jena. 1907. Describes tests in which with  $\text{Na}_2\text{SiO}_3$  taken as a standard,  $\text{FeSiO}_3$ ,  $\text{MnSiO}_3$ ,  $\text{Fe}_2(\text{SiO}_3)_3$ ,  $\text{MgSiO}_3$ , lowered the viscosity in the order named.  $\text{CaSiO}_3$  and especially  $\text{Al}_2(\text{SiO}_3)_3$  raised the viscosity.  $\text{SiO}_2$  raised the viscosity, and  $\text{B}_2\text{O}_3$  and  $\text{WO}_3$  lowered it. An apparatus similar to Tamman's was used.



51. HOFMAN, H. O. General metallurgy. 1913, pp. 433-470. Gives composition, formation temperatures, and melting temperatures of various silicate slags, with table and curves. Discusses physical properties.
52. HOWE, H. M. Notes on the use of the triaxial diagram and triangular pyramid for graphical illustration. Trans. Am. Inst. Min. Eng., vol. 28, 1898, pp. 346-354. States that formation temperature is higher than fusion temperature.
53. JOHNSON, J. E., JR. The effect of alumina in blast-furnace slags. Trans. Am. Inst. Min. Eng., vol. 44, 1912, pp. 123-142. Gives effect of  $\text{Al}_2\text{O}_3$  and  $\text{MgO}$  in blast-furnace slags. Considers influence of viscosity and methods of measuring it.
54. JUPTNER, H. The constitution of slags and the part they play in the metallurgy of iron. Jour. Iron and Steel Inst., vol. 58, pt. 2, 1900, pp. 276-310. Gives three main divisions of slags—silicates, phosphates, and oxides. Refers to work of Ledebur, Akermann, Gredt, Vogt, Hofman, and others.
55. ——— Grundzüge der Siderologie. Leipzig, Bd. 1, 1900, 315 pp.; Bd. 2, 1902, 408 pp. Gives table of slag minerals.
56. KONSTANTINOV, N., AND SÉLIVANOV, B. The artificial preparation and fusibility of iron calcium silicates. Ztschr. Kryst. u. Min., Bd. 55, 1915, p. 198; Chem. Abs., vol. 10, 1916, p. 441. Describes investigation of system  $\text{FeSiO}_3\text{-CaSiO}_3$  by thermal and optical methods.  $\text{FeSiO}_3$  crystallized well only when slowly cooled, and solidified at  $1,145^\circ$  to  $1,160^\circ$  C.
57. PERCY, JOHN. Metallurgy. London, 1875, pp. 46-86. Discussion of composition and physical properties of slags, mainly silicates.
58. PETERS, E. D. Principles of copper smelting. 1907, pp. 339-400. Describes practical study of slags, giving composition, melting temperatures, and formation temperatures of copper slags.
59. RANKIN, G. A., AND MERWIN, H. E. The ternary system  $\text{CaO-Al}_2\text{O}_3\text{-MgO}$ . Jour. Am. Chem. Soc., vol. 38, 1916, pp. 568-588. A physico-chemical study in which the method of quenching was used to determine the melting temperatures. Concentration-temperature models and equilibrium diagrams are given.
60. RANKIN, G. A., AND WRIGHT, F. E. The ternary system  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ . Am. Jour. Sci., vol. 39, 1915, pp. 1-79. A summary of the complete investigation of this system, giving tables of melting points of minerals, compounds, and eutectics, with triaxial diagrams and concentration-temperature models.
61. SÉLIVANOV, B. Préparation artificielle, fusibilité et quelques autres propriétés des silicates du système  $2\text{FeO} \cdot \text{SiO}_2 + 2\text{CaO} \cdot \text{SiO}_2$ . Rev. Soc. Russe Métal., 1915, p. 328; Rev. Métall., Extraits, t. 12, 1915, pp. 309-318. Chem. Abs., vol. 10, 1916, p. 1157. Describes preparation, fusibility, and some other properties of silicates of the system  $2\text{FeO} \cdot \text{SiO}_2\text{-}2\text{CaO} \cdot \text{SiO}_2$ . Weighed quantities of  $\text{FeO}$ ,  $\text{CaO}$ , and  $\text{SiO}_2$  were heated in a platinum boat to a certain temperature for a given time, in an atmosphere of nitrogen, and allowed to cool. As a result of heating, the  $\text{FeO}$  forms  $\text{Fe}$  and  $\text{Fe}_2\text{O}_3$  in some degree. No melting temperatures are given in abstract account.
62. SHEPHARD, E. S., AND RANKIN, G. A. The binary system of alumina with silica, lime, and magnesia. Am. Jour. Sci., vol. 28, 1909, pp. 293-333. Ztschr. anorg. Chem., Bd. 68, 1910, pp. 370-420. A thermal and microscopic study of the binary systems. Temperature-concentration diagrams are given, showing the melting points of compounds and eutectics.

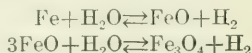


63. SOSMAN, R. B. The common refractory oxides. *Jour. Ind. and Eng. Chem.*, vol. 8, 1916, pp. 985-990. Summary of reliable data on melting and inversion temperatures, with diagrams of two and three component systems of the oxides  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ , and  $\text{FeO}$ .
64. SOSMAN, R. B., AND MERWIN, H. E. Preliminary report on the system lime-ferric oxide. *Jour. Wash. Acad. Sci.*, vol. 6, 1916, pp. 532-537. States that  $\text{Fe}_2\text{O}_3$  dissociates to some degree in all melted mixtures of  $\text{CaO}$  and  $\text{Fe}_2\text{O}_3$ , especially when the latter is in excess. Mixtures containing less than 50 molecular per cent  $\text{CaO}$  were not heated above  $1,250^\circ \text{C}$ .; only two binary compounds could be found,  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  and  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ .  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  dissociated at  $1,216^\circ \text{C}$ ., liquefying in part;  $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$  dissociated at  $1,436^\circ \text{C}$ ., liquefying in part.
65. TURNER, T. The physical and chemical properties of slags. *Jour. Soc. Chem. Ind.*, vol. 24, 1905, pp. 1142-1149. Presents record of experiments at University of Birmingham with blast-furnace slag, in which thermal method of obtaining cooling curves was used. Concludes that silicate slags are heterogeneous mixtures with no definite melting point to which the phase rule is applicable.
66. VOGT, J. H. L. *Die Silicateschmelzlösungen*. Christiania, vol. 1, 1903, 161 pp.; vol. 2, 1904, 235 pp. Volume 1 deals with minerals found in silicate fusions with special reference to the dependence of mineral formation upon the composition of the solution. Volume 2 deals with the lowering of the melting points of silicate fusions (comparable to lowering of freezing point in solutions by dissolved substance). A general study of slag and slag minerals from the point of view of the physical chemist.
67. WALLACE, R. C. Ueber die binären System des Natriumsilicats mit Lithium-, Magnesium-, Calcium-, Strontium-, und Barium-metasilicat; des Lithium metasilicats mit Kalium-, Magnesium-, Calcium-, Strontium-, und Barium-metasilicat; und über das Dreistoffsystem  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ . *Ztschr. anorg. Chem.*, Bd. 63, 1909, pp. 1-48. Presents cooling curves obtained by the thermal method; gives conclusions regarding solubility, eutectics, and different crystal phases, and discusses dissociation, decomposition, reduction, and oxidation of substances occurring in, or related to, coal ash and the formation of clinker.
68. BAUR, E., AND GLAESSNER, A. Gleichgewichte der Eisenoxyde mit Kohlenoxyd und Kohlensäure. *Ztschr. physik. Chem.*, Bd. 43, 1903, pp. 354-368. Discusses the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{FeO}$  and  $\text{FeO}$  to  $\text{Fe}$  by  $\text{CO}$ . Gives tables and curves of results of study of the following reactions:



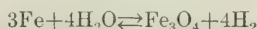
See pages 53 and 54, this bulletin.

69. CHAUDRON, G. Réactions réversibles de l'eau sur le fer et sur l'oxyde ferreux. *Compt. rend.*, t. 159, 1914, pp. 237-239. Gives two series of equilibrium data corresponding to following reactions:



See also pages 44 to 46 of this bulletin.

70. DEVILLE, H. ST. CLAIRE. Action de l'eau sur le fer et de l'hydrogène sur l'oxyde de fer. *Compt. rend.*, t. 70, 1870, pp. 1105-1111 and 1201-1207. Presents equilibrium data corresponding to reaction:



71. FALCKE, V. Die Reaktionen zwischen Eisenoxydul und Kohle und zwischen Kohlenoxyd und Eisen. *Ber. deut. chem. Gesell.*, Bd. 46, 1913, pp. 743-750. States that addition of amorphous carbon has no effect on the pressure produced when FeO (containing 0.5 per cent C) and Fe are heated together at 530° to 660° C., and that the reaction between FeO and CO is different when the CO is passed over the FeO than when the two are heated together in a closed vessel; in the reaction first mentioned much carbon is deposited; in the second reaction no carbon is deposited.
72. ———. Die Reaktionen zwischen Eisenoxydul und Kohle und zwischen Kohlenoxyd und Eisen. *Ztschr. Electrochem.*, Bd. 22, 1916, pp. 121-133; abstracted in *Jour. Chem. Soc.*, vol. 110, pt. 2, 1916, p. 484. Compares results obtained by author with those of Schenck.
73. GLASER, FERDINAND. Ueber Reduktion von Metalloxyden im Wasserstoffstrom. *Ztschr. anorg. Chem.*, Bd. 36, 1903, pp. 1-35. Treats of reduction of various metallic oxides (including Fe<sub>2</sub>O<sub>3</sub>) in current of hydrogen.
74. HILPERT, S. Ueber die Reduktion von Eisenoxyd durch Wasserstoff und Kohlenoxyd. *Ber. deut. chem. Gesell.*, Bd. 42, 1909, pp. 4575-4581. Temperatures are given for the beginning of reduction of iron oxide prepared by various methods. States that FeO and Fe<sub>3</sub>O<sub>4</sub> in a pure form could not be obtained, each sample showing at once all the stages of reduction. On reducing with CO the products were contaminated with C, seemingly in the form of cementite.
75. ———. Ueber die Sauerstoff-Abgabe des Eisenoxyd, bei hohen Temperaturen. *Ber. deut. chem. Gesell.*, Bd. 42, 1909, pp. 4893-4895. States that results varied according to source and previous treatment of oxide. The reaction took place slowly.
76. HILPERT, S., AND BEYER, J. Ueber Eisenoxyduloxys und Eisenoxydul. *Ber. deut. chem. Gesell.*, Bd. 44, 1911, pp. 1608-1619. Describes a method for preparing pure Fe<sub>3</sub>O<sub>4</sub> by heating Fe<sub>2</sub>O<sub>3</sub> in H<sub>2</sub> containing a definite amount of water vapor. Attempts to prepare FeO by increasing the amount of water vapor and raising the temperature always gave some Fe, and at 1,100° C. the product still contained 1.5 per cent Fe<sub>2</sub>O<sub>3</sub>. A method was devised for making comparative measurements of the magnetic properties of the products in powdered form. The presence of solid solutions with Fe<sub>3</sub>O<sub>4</sub> was shown.
77. HOFMAN, H. O., AND MOSTOWITSCH, W. The behavior of calcium sulphate at elevated temperatures with some fluxes. *Trans. Am. Inst. Min. Eng.*, vol. 39, 1908, pp. 628-653. Describes experiments made in platinum-foil furnace, in pure, dry air with fluxes, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and PbO (separately) with CaSO<sub>4</sub>. Hydrrous CaSO<sub>4</sub> loses its combined water at 900° C.; anhydrous CaSO<sub>4</sub> is unchanged to 1,200° C., where dissociation begins, with separation of SO<sub>2</sub> and O<sub>2</sub>, the rate and degree of dissociation depending on time and temperature. CaSO<sub>4</sub> fuses at 1,360° C., being somewhat decomposed. SiO<sub>2</sub> decomposes CaSO<sub>4</sub>, decomposition beginning at 1,000° C. and finishing at 1,250° C., products being CaO, SiO<sub>2</sub>, and gases. It appears that the formation temperature of calcium silicate lies below melting point. Pure Fe<sub>2</sub>O<sub>3</sub> begins to decom-

pose  $\text{CaSO}_4$  at  $1,100^\circ \text{C}$ ., decomposition ending at  $1,250^\circ \text{C}$ . A higher temperature is required than with  $\text{SiO}_2$ , but the action is more rapid. The decomposition product is  $\text{CaO} \cdot \text{Fe}_2\text{O}_3$  (calcium ferrite), which fuses at  $1,250^\circ \text{C}$ . This product can dissolve and decompose  $\text{CaSO}_4$ .

78. ———. The behavior of calcium sulphate at elevated temperatures with some fluxes. *Trans. Am. Inst. Min. Eng.*, vol. 40, 1909, pp. 807–808. Authors found that  $\text{Fe}_2\text{O}_3$  remained unchanged at  $1,360^\circ \text{C}$ . in dry air, but at  $1,375^\circ \text{C}$ . it lost  $\text{O}_2$  (4.4 per cent), became magnetic, and contained some  $\text{FeO}$ .
79. HOFMAN, H. O., AND WANJUKOW, W. The decomposition of metallic sulphates at elevated temperatures in a current of dry air. *Trans. Am. Inst. Min. Eng.*, vol. 43, 1912, pp. 523–577. Heated in current of pure, dry air,  $\text{FeSO}_4$  fuses to  $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ , which dissociates into  $\text{Fe}_2\text{O}_3$  and  $\text{SO}_3$ , noticeably at  $492^\circ \text{C}$ ., and markedly at  $550^\circ$  to  $560^\circ \text{C}$ .  $\text{Al}_2(\text{SO}_4)_3$  begins to dissociate at  $590^\circ \text{C}$ ., disassociation becoming marked at  $639^\circ \text{C}$ . Dissociation of  $\text{MgSO}_4$  begins at  $890^\circ \text{C}$ .
80. HOSTETTER, J. C., AND SOSMAN, R. B. The dissociation of ferric oxide in air. *Jour. Am. Chem. Soc.*, vol. 38, 1916, pp. 1188–1198. Describes experiments that showed a measureable dissociation of  $\text{Fe}_2\text{O}_3$  in air at all temperatures between  $1,100^\circ$  and  $1,300^\circ \text{C}$ . and indicated that dissociation increases with increase of temperature.
81. JOHNSON, W. MCA. The reducibility of metallic oxides as affected by heat treatment. *Trans. Am. Inst. Min. Eng.*, vol. 47, 1914, pp. 219–231. Discusses H. O. Hofman's experiments to determine comparative reducing effects of  $\text{CH}_4$ ,  $\text{CO}$ , illuminating gas, and producer gas on hard hematite. The tests showed that, irrespective of the reversibility of the reaction, the progress of the reduction was not simply a function of the time and the temperature.
82. JOHNSTON, JOHN. The thermal dissociation of  $\text{CaCO}_3$ . *Jour. Am. Chem. Soc.*, vol. 32, 1910, pp. 938–946. States that dissociation begins at  $587^\circ \text{C}$ . and is complete at  $898^\circ \text{C}$ ., at atmospheric pressure.
83. KINNISON, C. S. A note on the reduction of  $\text{Fe}_2\text{O}_3$ . *Trans. Am. Cer. Soc.*, vol. 16, 1914, pp. 136–143. The reaction  $3\text{Fe}_2\text{O}_3 \rightleftharpoons 2\text{Fe}_3\text{O}_4 + \text{O}_2$  in clays was studied by adding 5 per cent  $\text{Fe}_2\text{O}_3$  in the form of  $\text{Fe}_2(\text{OH})_6$  to kaolin and various mixtures of  $\text{SiO}_2$  and kaolin and heating the mixture until a black color developed. Author concludes that (1) the smaller the  $\text{Al}_2\text{O}_3$ – $\text{SiO}_2$  ratio the lower the temperature of formation of "ferrous silicate"; (2) at comparatively low temperatures fluxes augment the coloring power of iron; and (3) in mixtures with large amounts of fluxes, "reduction is associated with solution." The dissociation temperature is about  $1,210^\circ$  to  $1,220^\circ \text{C}$ . Fluxes contribute to lowering of the transition point.
84. KREMANN, R. K. The application of physico-chemical theory to technical processes and manufacturing methods. London, 1913, pp. 115–131. Gives equilibrium data on the systems of Fe and its oxides and of C and its oxides.
85. MATHESIUS, LUDWIG. Untersuchungen über die Reduzierbarkeit von Eisenerzen in strömenden Gasen. *Stahl und Eisen*, Bd. 34, 1914, pp. 866–872. Describes method for determination of Fe,  $\text{Fe}''$ ,  $\text{Fe}'''$ . Ores were heated at  $600^\circ$ ,  $700^\circ$ , and  $900^\circ \text{C}$ . in a current of illuminating gas. Concludes that true equilibrium is not reached in a moving gas stream and that the degree of reduction is largely dependent on the nature of the ore and the exposed surface. Reduction is difficult in a sintered product.



86. PREUNER, G. Das Gleichgewicht zwischen Eisen, Eisenoxyduloxyd, Wasserstoff und Wasserdampf. *Ztschr. phys. Chem.*, Bd. 47, 1904, pp. 385-417. Gives equilibrium data for system Fe, Fe<sub>3</sub>O<sub>4</sub>, H<sub>2</sub>, and H<sub>2</sub>O. (See pp. 44-46 of this bulletin.)
87. RHEAD, T. F. E., AND WHEELER, R. V. The effect of temperature on the equilibrium  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ . *Jour. Chem. Soc.*, vol. 97, 1910, pp. 2178-2179. Wood charcoal was heated 48 to 240 hours at temperatures of 850° to 1,200° C., and the equilibrium constant K was calculated at the various temperatures from the analysis of the resulting gases.
88. ——— The effect of temperature and of pressure on the equilibrium  $2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$ . *Jour. Chem. Soc.*, vol. 99, 1911, pp. 1140-1153. Tables are given showing the composition of the resulting gases at temperatures of 800° to 1,100° C. and pressures of 1.11 to 1.33 atmospheres.
89. ——— The rate of reduction of carbon dioxide by carbon. *Jour. Chem. Soc.*, vol. 101, 1912, pp. 831-845. Critical discussion of results of other investigators. Concludes that in manufacture of producer gas temperatures should be 1,100° C. or more to insure reduction of CO<sub>2</sub> to CO.
90. SCHENCK, RUDOLPH. *Physikalische Chemie der Metalle*. Halle, 1909, 193 pp. Pages 112 to 136 are on oxidation and reduction; pages 137 to 165 treat of blast-furnace gases and equilibrium of various systems, such as CO<sub>2</sub>, CO, C, Fe, Fe<sub>2</sub>O<sub>3</sub>, etc.
91. SOSMAN, R. B. Some problems of the oxides of iron. *Jour. Wash. Acad. Sci.*, vol. 7, 1917, pp. 55-72. Reviews present knowledge regarding the oxides of iron relative to the phase rule. Discusses the relation of iron oxides to certain geological problems.
92. SOSMAN, R. B., AND HOSTETTER, J. C. The oxides of iron. 1. Solid solutions in the system Fe<sub>2</sub>O<sub>3</sub>-Fe<sub>3</sub>O<sub>4</sub>. *Jour. Am. Chem. Soc.*, vol. 38, 1916, pp. 807-833. Reports investigation undertaken as basis for study of iron-bearing silicates at high temperatures, giving results of measurements of dissociation pressures of the iron oxides made in vacuum furnace.
93. ———. The reduction of iron oxides by platinum, with a note on the susceptibility of iron-bearing platinum. *Jour. Wash. Acad. Sci.*, vol. 5, 1915, pp. 293-303. States that platinum acts on hematite and magnetite at 1,200° C. under low O<sub>2</sub> pressures, absorbing Fe and giving off O<sub>2</sub>; reacts in the same way with magnetite at 1,600° C. and O<sub>2</sub> at atmospheric pressure.
94. STOFFEL, A. Ueber die Reaktion zwischen Kohlenoxyd und Eisen. *Ztschr. anorg. Chem.*, Bd. 84, 1914, pp. 56-76. Reports results of a study of velocity of formation of Fe(CO)<sub>5</sub> from Fe and CO and effect of various factors on the velocity. When CO was passed over Fe powder at a pressure of 1 atmosphere the reaction was at first rapid, becoming slower as the amount of CO absorbed increased, but still continuing after one week. Decomposition occurred above 60° to 70° C. and was complete at 100° C.
95. WALDEN, P. T. On the dissociation pressure of ferric oxide. *Jour. Am. Chem. Soc.*, vol. 30, 1908, p. 1350. Author determined the pressure curve corresponding to the reaction  $3\text{Fe}_2\text{O}_3 \rightleftharpoons 2\text{Fe}_3\text{O}_4 + \text{O}$ . At about 1,350° C. the pressure was found to be 160 mm.
96. WARTENBERG, H. von. Ueber die Reduktion der Kieselsäure. *Ztschr. anorg. Chem.*, Bd. 79, 1912, pp. 71-87. States that partial pressure of Si vapor, assuming that it is monatomic, is  $3 \times 10^{-3}$  at 1,315° C., and that SiO<sub>2</sub> is reduced and sublimes in H<sub>2</sub> and also in CO at 1,350° to 1,400° C.



# MELTING AND SOFTENING TEMPERATURES OF OXIDES, SULPHIDES, SILICATES, MIXTURES, AND SLAGS.

97. AKERMANN, R. Ueber die Bildungstemperaturen der Hochofenschlacken. Stahl und Eisen, Jahrg. 10. 1890, pp. 424-425; abstracted in Jour. Iron and Steel Inst., 1890, pt. 2, p. 760. Discusses Gredt's determinations of the formation temperatures of slags and compares his results with those obtained by the calorimetric method. The latter method gave lower results. Gives the specific heat of blast-furnace slags as between 0.29 and 0.33.
98. BECKER, E. Ueber das Zustandsdiagramm Schwefel-Eisen und den durch Schwefel hervorgerufenen Rotbruch. Stahl und Eisen, Bd. 32, 1912, pp. 1017-1021; abstracted in Jour. Iron and Steel Inst., vol. 86, pt. 2, 1912, pp. 604-605. Deals with equilibrium of the system iron-sulphur; gives eutectic mixture as 84.6 per cent iron sulphide and 15.4 per cent iron, melting at 985°.
99. BISHOP, CARL. Relative Schmelzbarkeit der Silikate des Eisens, des Kalks, der Magnesia und der Thonerde. Dingl. poly. Jour., Bd. 165, 1862, pp. 378-381. Gives relative fusibilities of iron and lime silicates.
100. BLEININGER, A. V., AND BROWN, G. H. The testing of clay refractories, with special reference to their load-carrying capacities at furnace temperatures. Tech. Paper No. 7, U. S. Bureau of Standards, 1911, 78 pp. Discusses Seger cones and their uses; influence of viscosity; and effects of various constituents of fire clays upon the softening temperatures. See also No. 42.
101. BODOUARD, O. Experiments on the fusibility of slags. Jour. Iron and Steel Inst., vol. 67, 1905, pp. 339-382. Fletcher gas furnace was used for temperatures up to 1,450° C., and Deville furnace for higher temperatures. Gives softening temperatures of silicates of  $Al_2O_3$  and of  $CaO$ ; of aluminates of  $CaO$ ; and of aluminocalcic silicates. Results are represented by triaxial diagrams. Also gives softening temperatures of a number of industrial slags.
102. COBB, J. W. The synthesis of a glaze, glass, or other complex silicate. Jour. Soc. Chem. Ind., vol. 29, 1910, pp. 69-74, 250-259, 333-336, 399-404, 608-614, 799-802. Experiments were performed in laboratory muffle furnace and in large works furnace. Draws conclusions on progress of slag formation by determining ingredients that were (1) "quickly soluble" ( $SiO_2$ ,  $CaO$ , etc., extracted by  $N-HCl$  in one hour), (2) "slowly soluble" (successive treatment with  $N-HCl$ , 24-hour periods, until only trace resulted) and (3) "silica soluble in  $Na_2CO_3$ " ( $SiO_2$  extracted by hot 5 per cent  $Na_2CO_3$  in 15 minutes). Describes physical condition or degree of progress toward fusion. Gives results with two samples of broken glassware.
103. DAY, A. L., AND SOSMAN, R. B. The melting points of minerals in the light of recent investigations on the gas thermometer. Am. Jour. Sci., vol. 31, 1911, pp. 341-349. Gives a series of melting points, with bibliography.
104. DITTLER, EMIL. The melting points of potassium-sodium feldspars. Tech. Min. Petr. Mittl., Bd. 31, 1914, pp. 513-522; Keram. Rundschau., Bd. 21, 1914, pp. 390-391; Chem. Abs., vol. 8, 1914, p. 222. Presents table showing chemical analysis and mineralogical constitution of feldspars used and their fusion temperatures. Melting points of albite silicates lowered by addition of orthoclase silicates up to 40 to 43 per cent of latter; with larger proportion the melting point is raised.

105. FLACH, G. Ueber die Wirkung von Metalloxyden auf den Schmelzpunkte von Quarz-Zettlitz-Kaolin-Mischungen. *Sprechsaal*, Jahrg. 44, 1911, pp. 171-173, 187-189, 205-207, 219-220, and 626. Gives tables showing effects of various oxides, among them  $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{FeO}$ , on mixtures of quartz and Zettlitz kaolin. Temperature measurements expressed in terms of Seger cones. Revision of works of Richter, Bishof, Seger, and others.
106. FRENCH, A. T. Some analyses of copper blast furnace slags and determinations of their melting points. *Mining Sci.*, vol. 61, 1910, pp. 133-134. Used muffle furnace and Seger cones; did not consider temperature even throughout muffle. Results, for a series of 10 slags, show that slag of highest melting point contained most  $\text{Al}_2\text{O}_3$  and that slag of lowest melting point contained least  $\text{Al}_2\text{O}_3$ .
107. FULTON, C. H. The constitution and melting points of a series of copper slags. *Trans. Am. Inst. Min. Eng.*, vol. 44, 1912, pp. 751-780. Used a carbon-resistance furnace and, by thermal method, determined melting points of a number of copper slags. Concludes that slags of lowest melting points lie between 1.4 and 1.65, silicate degree.
108. GREDT, PAUL. Ueber die Bildungs-temperaturen der Hochofenschlacken. *Stahl und Eisen*, Bd. 9, 1889, pp. 756-759. Gives formation temperatures of a number of synthetic blast-furnace slags, composed of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{CaO}$ , and  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ , and  $\text{MgO}$ . Expresses temperatures in terms of Seger cones.
109. HOFMAN, H. O. Some experiments determining the refractoriness of fire clays. *Trans. Am. Inst. Min. Eng.*, vol. 24, 1894, pp. 42-66. He states that Seger cones are not true pyrometers, as the change from a mixture to a compound is not a function of temperature alone, but depends also on the manner of firing, the time of heating, and the form of furnace.
110. ———. The temperatures at which certain ferrous and calcic silicates are formed in fusion, and the effect upon these temperatures of the presence of certain metallic oxides. *Trans. Am. Inst. Min. Eng.*, vol. 29, 1899, pp. 682-721. Describes softening-temperature determinations made in a gas furnace having a reducing atmosphere, the slag mixture being molded into small cones,  $\frac{3}{8}$  by  $\frac{3}{8}$  inch, and the temperatures being measured with Seger cones. Gives table showing effect on softening point of replacing  $\text{SiO}_2$  with  $\text{Al}_2\text{O}_3$  (temperature increases with increase of  $\text{Al}_2\text{O}_3$ ); also table showing effect of replacing  $\text{FeO}$  and  $\text{CaO}$  with  $\text{Al}_2\text{O}_3$ .
111. HOFMAN, H. O., AND STOUGHTON, B. Does the size of the particle have any influence in determining the resistance of fire clays to heat and to fluxes? *Trans. Am. Inst. Min. Eng.*, vol. 28, 1898, pp. 440-444. Concludes that, as tables show only slight difference in temperature of fusion between pulverized and rough samples, the laboratory method of grinding to a powder will give results directly comparable with those obtained in practice on larger and coarser samples.
112. HOWE, H. M. Preliminary note on the thermal properties of slags. *Trans. Am. Inst. Min. Eng.*, vol. 18, 1890, pp. 724-747. Used a gas furnace and calorimetric method of determining temperature. Gives softening temperatures of various  $\text{CaO}$ ,  $\text{MgO}$ , and  $\text{SiO}_2$  mixtures, both with and without previous heating to higher temperature. Gives melting point of  $\text{CaO.SiO}_2$  as  $1,381^\circ \text{C}$ . Thinks that formation temperatures are higher than melting temperatures.

113. ———. Metallurgical laboratory notes. Boston Testing Laboratories, Boston, 1902, pp. 46–69. Discusses melting points of silicates. Uses cone method, making pyramid with  $\frac{3}{4}$ -inch base and  $1\frac{1}{2}$  inches high, of 100-mesh material, with a binder of 10 to 15 per cent vaseline mixed with heavy lubricating oil.
114. JOHNSON, W. McA. A new apparatus for determining the melting points of slags. Jour. Chem. Met. Min. Soc. South Africa, vol. 7, 1906–7, p. 98. Slag allowed to drop through hole in cylinder of Acheson graphite.
115. KANOLT, C. W. Melting points of fire bricks. Tech. Paper No. 10, U. S. Bureau of Standards, 1912, 17 pp. Gives melting points of 54 samples of fire bricks, including fire clay, bauxite, silica, magnesia, and chromite brick, determined in Arsen vacuum furnace with Morse optical pyrometer. Melting points were as follows: Kaolin,  $1,740^{\circ}$  C.; pure  $\text{Al}_2\text{O}_3$ ,  $2,010^{\circ}$  C.; pure  $\text{SiO}_2$ ,  $1,750^{\circ}$  C.; bauxite,  $1,820^{\circ}$  C.; bauxite clay,  $1,795^{\circ}$  C.; and chromite,  $2,180^{\circ}$  C.
116. ———. Melting points of some refractory oxides. United States Bureau of Standards Bull., vol. 10, No. 2, 212, 1914, pp. 295–314. With same methods as described in Technologic Paper 10, author determined following melting points:  $\text{MgO}$ ,  $2,800^{\circ}$  C.;  $\text{CaO}$ ,  $2,572^{\circ}$  C.;  $\text{Al}_2\text{O}_3$ ,  $2,050^{\circ}$  C.;  $\text{Cr}_2\text{O}_3$ ,  $1,990^{\circ}$  C.; and Pt,  $1,755^{\circ}$  C.
117. KULTASCHIEFF, N. V. Ueber die Schmelzpunkte von Calciumsilikat ( $\text{CaSiO}_3$ ), Natriumsilikat ( $\text{Na}_2\text{SiO}_3$ ) und ihren Mischungen. Ztschr. anorg. Chem. Bd. 35, 1903, pp. 187–193. Gives tables of melting points, from pure  $\text{Na}_2\text{SiO}_3$  at  $1,007^{\circ}$  C. to mixture of 15 per cent  $\text{Na}_2\text{SiO}_3$  and 85 per cent  $\text{CaSiO}_3$  at  $1,150^{\circ}$  C. (Melting pure  $\text{CaSiO}_3$  above  $1,400^{\circ}$  C). Used thermal method in getting freezing-point curve.
118. LEITMEIER, H. VON. Zur Kenntnis der Schmelzpunkte von Silikaten. Der Einfluss der Korngrösse auf den Schmelzpunkte. Bestimmung des Schmelzpunktes einiger Silikate durch längeres Erhitzen. Ztschr. anorg. Chem. Bd. 81, 1913, pp. 209–232. Used Heraeus platinum furnace, with thermocouple. Gives sintering and melting points for series of natural minerals, showing influence of size of particles. Difference for coarse (3 to 4 mm. diameter) and fine (40 mm. in diameter) particles ranged up to  $70^{\circ}$  C. Leitmeier's melting temperatures are really softening temperatures, that is, none represent the equilibrium point of solid liquid.
119. LOEBE, R., AND BECKER, E. Das System Eisen-Schwefeleisen. Ztschr. anorg. Chem., Bd. 77, 1912, pp. 301–319. The two components form no mixed crystals, though Fe may be slightly soluble in FeS. Melting point of FeS is  $1,198^{\circ}$  C.
120. MATHESIUS, W. Die Entstehung der Schlacken in hüttenmännischen Prozessen; die Konstitution der Schlacken, ihre industrielle Verwertung. Stahl und Eisen, Bd. 24, 1904, pp. 1000–1007. Discusses origin and utilization of slags; does not give formation or melting points or results of original work.
121. NACKEN, R. Vergleich der optischen und der thermischen Methode zur Bestimmung von Schmelz-temperaturen. (Compares optical and thermal methods for the determination of melting points.) Centralbl. Min. Geol., 1913, pp. 328–337; Chem. Abs. vol. 7, 1913, p. 3097. Shows discrepancies existing in values given in literature. Author states that by great care he obtained optical results that agree well with those obtained by thermal method.



122. ———. Ueber die Bestimmung der Schmelz-temperaturen von Silikaten auf optischen Wege (determination of fusion temperature of silicates by an optical method). *Silikat Ztschr.*, Jahrg. 1, 1913, pp. 65–67; *Chem. Abs.*, vol. 7, 1913, p. 4053. Substance was heated in platinum-resistance furnace, and observations were made through polarizing microscope; melting point is given as temperature at which interference colors disappear.
123. RIEKE, R. Das Richters'sche Gesetz. Ein Beitrag zur Kenntnis der Flussmittelwirkung. *Sprechsaal*, Jahrg. 43, 1910, pp. 198–199, 214–216, 229–232. Discusses an extensive investigation of the fluxing action of the basic oxides, used in the ceramic industries, on Zettlitz kaolin and mixtures of quartz and kaolin. The raw materials, as kaolin, quartz, limestone, iron oxide, etc., were ground wet in a ball mill. Some of the mixtures were ground dry, ignited in a kiln, and again ground. The softening points of the mixtures were determined in a carbon resistance furnace by comparison with standard pyrometric cones.
124. ———. Ueber die Schmelz-barkeit von Kalk-Tonerde-Kieselsäure Mischungen. *Stahl und Eisen*, Bd. 28, 1908, pp. 16–19; *Abs. Jour. Soc. Chem. Ind.*, vol. 27, 1908, p. 123. Discusses fusibility of lime-alumina-silica mixtures. The mixture was molded into small cones, and the softening points were measured by Seger cones. Mixtures with more than 50 per cent CaO crumbled into powder when cooled slowly.
125. RUFF, OTTO. Arbeiten im Gebiet hoher Temperaturen: Ueber das Schmelzen und Verdampfen unserer feuerbeständigsten Oxyde im elektrischen Vakuumofen. *Ztschr. anorg. Chem.*, Bd. 82, 1913, pp. 373–400. Further work on material mentioned in No. 126 following.
126. ———. Ueber einen elektrischen Vakuumofen. *Ber. Deut. Chem. Gesell.*, Bd. 43, 1910, pp. 1564–1574. Describes carbon-tube-resistance vacuum furnace and its uses in melting and vaporizing oxides. Gives melting points, as follows: Pt, 1,745° to 1,755° C.; kaolin, 1,912° C.; and  $\text{Al}_2\text{O}_3$  (in  $\text{N}_2$ ), 2,065° C.
127. RUFF, O., AND GOEKE, O. Ueber das Schmelzen und Verdampfen unserer sogenannten hochfeuerfesten Stoffe. *Ztschr. angew. Chem.*, Bd. 24, 1911, pp. 1459–1465. Discusses investigations on the melting and vaporization of highly refractory materials. An electric vacuum furnace and a Wanner pyrometer were used. Gives melting point of  $\text{Al}_2\text{O}_3$  at 2,020° C.
128. SEGER, H. A. Collected writings; translated by members of the American Ceramic Society and edited by A. V. Bleining. Easton, Pa., 1902, 2 vols., 1157 pp. Pages 519 to 520 are on "The effect of titanitic acid on the fusibility of fire clays"; author considers that  $\text{TiO}_2$  has greater fluxing power than  $\text{SiO}_2$ . Pages 1005 to 1027 give data on use of Seger cones.
129. SMOLENSKY, S. Schmelzversuche mit Bisilikaten und Titanaten. *Ztschr. anorg. Chem.*, Bd. 73, 1911–12, pp. 293–303. States that thermal method was used to determine melting points of various mixtures of  $\text{CaSiO}_3$  and  $\text{CaTiO}_3$ ,  $\text{BaSiO}_3$ , and  $\text{BaTiO}_3$ , and  $\text{MnSiO}_3$  and  $\text{MnTiO}_3$ . A kryptol resistance furnace and a Pt–PtRh thermocouple were used. In general, the addition of  $\text{TiO}_2$  lowered the melting point.
130. SPRECHSAAL KALENDER. Schmelzpunkte. Jahrg. 8, Coburg, 1916. Gives melting points of oxides, silicates, and various mixtures.



131. STEFFE, HERMAN. Ueber die Bildungstemperaturen einiger Eisenoxydul-Kalkschlacken und einiger kalkfreien Eisenoxydul-schlacken, deren Kenntniss für das Verschmelzen der Bleierze Bedeutung hat. Dissertation. Berlin, 1906. Gives formation temperatures of some ferro-calcic and ferrous slags. Observations made of sintering temperature of mixture when heated in a platinum boat in a current of nitrogen. Temperatures were measured with thermocouple.
132. STEIN, G. Ueber die Darstellung einiger Silikate. *Ztschr. anorg. Chem.*, Bd. 55, 1907, pp. 159-174. The optical method, with Wanner pyrometer, was used for determining melting and inversion points of various silicates ( $\text{Al}_2\text{O}_3$ ,  $\text{FeO}$ , etc.). Discusses formation of Ca, Sr, and Ba carbides in the presence of  $\text{SiO}_2$ .
133. TREITSCHKE, W., AND TAMMANN, G. Ueber das Zustands-diagramm von Eisen und Schwefel. *Ztschr. anorg. Chem.*, Bd. 49, 1906, pp. 320-335. Determines cooling curve by thermal method, obtaining two "stop points"—one at  $970^\circ \text{C}$ . and one at  $1,400^\circ \text{C}$ .
134. WHITE, W. P. Melting-point determinations. *Am. Jour. Sci.*, vol. 28, 1909, pp. 453-473. Gives theoretical and mathematical considerations regarding the thermal method for determining melting points. Cites reasons for the variations that have been observed and mentions precautions.
135. ———. Melting-point methods at high temperatures. *Am. Jour. Sci.*, vol. 28, 1909, pp. 474-489. Describes furnace and thermo elements used, giving best methods for making melting-point determinations up to  $1,600^\circ$ .
136. ANONYMOUS. Formation temperatures of ferrous oxide-lime-silica slags. *Trans. Am. Inst. Min. Eng.*, vol. 31, 1901, p. 862; curves plotted from Hofman's paper. *Trans. Am. Inst. Min. Eng.*, vol. 29, 1899, pp. 682-721, showing effect on fusion temperature of replacing  $\text{CaO}$  by  $\text{MgO}$  and slag constituents by  $\text{Al}_2\text{O}_3$ . See also No. 63.
137. ———. Schmelzpunkte von Oxygen, Silikaten, Boraten und Aluminaten und deren eutektischen Gemischen. *Sprechsaal*, Jahrg., 44, 1911, pp. 710-713, 729-731, and 744-746. Presents, from various sources, a tabulation of results conveniently arranged.

#### PYROMETRIC CONES; THEIR USE IN MEASURING TEMPERATURE.

138. AMERICAN CERAMIC SOCIETY. Report of committee on Seger cones. *Trans.*, vol. 3, 1901, pp. 180-192. The committee was appointed to investigate reasons for unsatisfactory behavior of low-melting cones, mainly those containing  $\text{Fe}_2\text{O}_3$ . Suggests that boric acid, affected by S in the gas, and perhaps  $\text{CaCO}_3$ , changed to  $\text{CaSO}_4$  by S in gas may be the cause of trouble.
139. ASHLEY, H. F. A comparison of the various makes of Seger cones on the market. *Trans. Am. Cer. Soc.*, vol. 8, 1906, pp. 159-167. Compares German, English, and various American makes of cones in 48-hour burns in ceramic kilns.
140. BROWN, G. H., AND MURRAY, G. A. The function of time in the vitrification of clays. *Tech. Paper No. 17*, U. S. Bureau of Standards, 1913, 26 pp. Shows that rate of heating has decided bearing on the softening points of Seger cones and, in general, that the effect of time in firing of clay products is important.

141. GEIGSBECK, S. The fusing points of Seger cones expressed in degrees. Trans. Am. Cer. Soc., vol. 6, 1904, pp. 94-108. Discusses the advisability of expressing the melting points of cones in degrees. Orton and others opposed to such procedure.
142. ———. The melting points of pyrometric cones under various conditions. Trans. Am. Cer. Soc., vol. 14, 1912, pp. 849-871. Concludes that rate of heating has much to do with melting points of Seger cones and that they can not be used for measuring temperature.
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of solid and liquid copper was measured with thermocouple and various optical pyrometers.

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164. CLERC, L., AND MINET, A. Sur un nouveau four électrique à arc, applicable aux recherches de laboratoire. *Compt. rend.*, t. 146, 1908, p. 227; *Moniteur Sci.*, t. 22, 1908, p. 154. Describes an electric-arc furnace of 1 to 2 kilowatt capacity, manufactured in Paris.
165. ———. Untersuchungen über den elektrischen Öfen. *Electrochem. Ztschr.*, Bd. 15., 1908, pp. 97–100; *Chem. Abs.*, vol. 2, 1908, p. 3196. Describes an arc furnace, Moisson type, with values for current, voltage, etc.
166. COLHANE, D. F., AND BARD, E. E. An efficient electric furnace for high temperatures. *Met. and Chem. Eng.*, vol. 10, 1912, pp. 461–463. A carbon-resistance furnace, external parts of cement, refractories of alundum. Current consumption,  $\frac{1}{2}$  to 1 kilowatt.
167. DAY, A. L., AND ALLEN, E. T. Temperature measurements up to 1,600° C. *Phys. Review*, vol. 19, 1904, pp. 177–186. Describes platinum-wire (internal winding) vertical furnace for melting-point determinations.
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174. JEFFRIES, ZAY. Notes on the granular electric furnace. *Met. and Chem. Eng.*, vol. 12, 1914, pp. 154–157. Describes a convenient type of carbon-resistance furnace, with a resistor of kryptol, granular carbon or graphite, and alundum refractories. Approximately 3 kilowatts is required to attain temperature of 1,600° C.
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metal case, with a heating space 12 inches long by  $1\frac{1}{8}$  inches in diameter. Maximum capacity, 170 amperes at 23 volts. Used for study of properties of metals at high temperatures.

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187. WINN, R., AND DANTSIZEN, C. Small electric furnace with heating element of ductile tungsten or ductile molybdenum. *Jour. Ind. and Eng. Chem.*, vol. 3, 1911, pp. 770–771. Discusses construction of two types—vertical, crucible type, and horizontal, tube type, each with resistor of ductile tungsten or molybdenum wire protected from oxidation by an atmosphere of  $H_2$ .

See also Nos. 13, 46, 62, 126.

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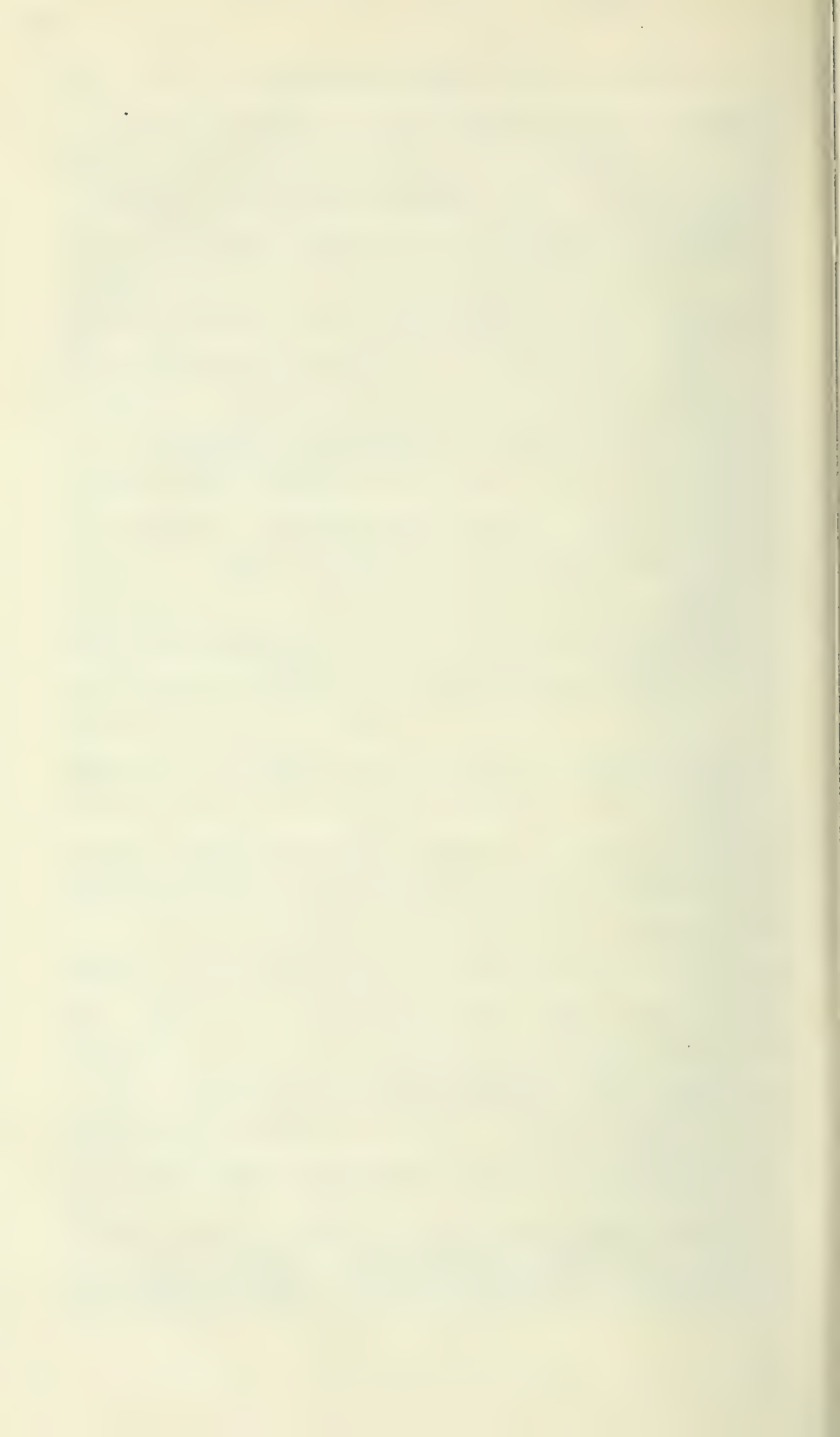
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# INDEX.

A.	Page.		Page.
Alabama, coal from, ash analyses of.....	27	Ash cones, effect of size of, on softening	
Alaska, coal from, ash analyses of.....	28	temperature of.....	32, 103, 104
Allison, V. C., acknowledgment to.....	118	on melting temperature of, figure	
Alumina, melting point of.....	15	showing.....	105
American bed, Ala., coal from, ash analysis	27	fluid temperature of, determination	
Anderson bed, Oreg., coal from, ash analysis		of.....	108
of.....	26	from Northrup furnace, appearance of...	43
Arkansas, coal from, ash analyses of.....	28	fused, appearance of, figure showing..	42,
Ash, alumina in.....	25	83, 84, 85	
carbon in, effect of on softening temper-		carbides in, formation of.....	47
ature of.....	115	iron content of.....	65
figure showing.....	70, 71	state of.....	64
containing Fe <sub>2</sub> O <sub>3</sub> , softening temperature		magnetism of.....	73
of.....	68	heating of, standard method for.....	112
composition of.....	13	preparation of, standard method for....	111
definition of.....	13	softening interval of, definition of.....	109
deformation point of, definition of.....	30	softening points of.....	34, 35
extraneous, nature of.....	14	softening temperature of, in different at-	
fineness of, effect of on softening temper-		mospheres.....	63, 68
ature of.....	114	figure showing.....	57, 58, 59, 60
fusing temperature of, variations in.....	1	softening temperature tests of, results of.	61, 82
ignition of in oxygen, furnace for, figure		swelling of, causes of.....	86
showing.....	102	vertical position of, advantages of.....	86
method of.....	101	See also Cones, Seger Cones.	
inherent, nature of.....	14	Atmospheres. See Reducing atmospheres.	
intrinsic, nature of.....	13	Augustine, C. E., cited.....	53, 55
iron in.....	25		
effect of on fusibility of.....	21	B.	
reduction of.....	110	Bailey, E. G., on determination of fusing	
lime in.....	25	temperature of ash.....	4
method of fusion of.....	10	Bibliography.....	119-138
preparation of, for fusibility tests.....	29	Binder, dextrin, effect of, on fusibility of ash	
silica in.....	25	cones.....	36
softening of, effect of iron content on....	21	Bleininger, A. V., acknowledgment to.....	117
factors influencing.....	20	Bureau of Mines, work of.....	1
importance of data on.....	1		
in hydrogen and water vapor mix-		C.	
tures.....	50	Carbides in fused cones, formation of.....	67
standard method of determining, im-		Carbon, unburned, effect of, on softening of	
portance of.....	44	ash.....	87, 115
Ash cones, appearance of in softening, figure		See also Ash.	
showing.....	31	Carbon dioxide and carbon monoxide atmos-	
critical temperatures in heating of, figure		pheres, difficulty in making tests	
showing.....	108	with.....	73
deformed, views of.....	43	effect of, on melting temperature of ash..	82, 116
effect of fineness of ash on fusibility of...	33	Carbon dioxide used in tests, preparation of.	55
of furnace atmospheres on softening		Carbon-resistance furnace, reducing atmos-	
temperature of.....	116	phere in.....	39
of inclination on softening tempera-		results of tests in.....	32
ture of.....	33	figure showing.....	40
of position on softening tempera-		See also Furnace, carbon-resistance.	
ture of.....	80	Carbon monoxide, reduction of iron in at-	
of rate of heating on softening tempera-		mosphere of.....	38, 39
ture of.....	35	used in tests, preparation of.....	55
of rate of heating on softening tempera-		Calcite in coal, occurrence of.....	14
ture of.....	56, 115	Calkins, W. B., determination of fusing tem-	
figure showing.....	34, 35, 106	perature of ash by.....	4
of shape of, on softening tempera-		Carney bed, Wyo., coal from, ash analysis of..	28
ture of.....	103, 104		

	Page.		Page.
Chaudron, G., on equilibria of iron and its oxides in hydrogen and water vapor.....	45	Flowing interval, definition of.....	113
China, coal from, ash analyses of.....	28	Fluid temperature, definition of.....	112
Clement, J. K., cited.....	55	determination of.....	108
Clinker, iron content of.....	65	Frazer, J. C. W., cited.....	55
view of.....	66	Freeport bed, Pa., coal from ash, analysis of.....	28
Clinkering of ash in coal, causes effecting.....	4,	Furnace, carbon-resistance, figure showing....	24
6, 21, 44		for fusibility tests, requirements of.....	89
relation of melting interval to.....	18	gas, reduction of iron in ash cones in....	38
relation of softening temperatures to.....	63	tests with, description of.....	92
Clinker slags, state of iron in.....	64	discussion of.....	110
Coal, impurities in, float-and-sink method for separation of.....	13	molybdenum, figure showing.....	23
silica in, occurrence of.....	14	Northrup, figure showing.....	25
Coals tested for ash fusibility, source of.....	26	silica-tube, figure showing.....	46, 47
See also States and beds named.		softening points of ash in, figure showing.....	38
Coal ash, analyses of.....	87	See also Carbon-resistance, molybdenum, platinum, Northrup, Meker, melder's, and Heraeus furnace.	
mixtures, analyses of.....	82	Fusiometer, description of.....	10
See also Ash.		Fusion temperature, methods used in determining.....	30
Coal Creek bed, Tenn., coal from, ash analysis of.....	27, 28	Fusion point, definition of.....	30, 50
Cobb, J. W., determination of fusing temperature of ash by.....	3		
Cones, "down point" of, values for.....	82	G.	
electromagnet for testing, figure showing.....	95	Gas, artificial, results of melting temperature tests with.....	98
position of, effect on softening temperature of.....	114	analysis of.....	100
shape of, effect on softening temperature of.....	115	natural, analysis of.....	100
size of, effect on softening temperature of.....	114	Gas furnace, advantages of.....	89
See also Ash cones, Seger cones.		atmosphere in, analyses of.....	93, 94
Constam, E. J., determination of melting temperature of ash by.....	6	Goodwin, E. G., acknowledgment to.....	118
Crucibles, for standard tests of fusibility, description of.....	113	Greiner, E., cited.....	21
		Gypsum in coal, occurrence of.....	14
D.			
Day, A. L., cited.....	18, 19	H.	
on melting point of minerals.....	15	Hall, A. E., cited.....	32
Deformation point, definition of.....	30, 50	Heraeus furnace, figure showing.....	22
Dennis, L. M., cited.....	55	saturation for, figure showing.....	47, 48
Depew, H. A., acknowledgment to.....	118	Hill, H. H., acknowledgment to.....	118
Deville, S. C. H., cited.....	44	Hitchcock, E. A., boiler test of coals by.....	4
Dextrin binder, effect of, on fusibility of ash cone.....	36	Hubley, F. C., on determination of fusibility of ash.....	9
"Down point," definition of.....	81	Hulett, G. A., acknowledgment to.....	117
values for.....	82	Hydrogen, equilibrium of with water vapor, iron, and iron oxides.....	44, 45
E.		fusibility of ash cones in, figure showing.....	34
Electromagnet, for testing fused cones, figure showing.....	95	use of, in fusibility tests.....	49
England, coal from, ash analysis of.....	28	Hydrogen and water-vapor atmosphere, effect of on softening temperature of ash..	116
Equilibrium data in the system CO, CO <sub>2</sub> , Fe, FeO, Fe <sub>2</sub> O <sub>4</sub> , figure showing.....	53	preparation of.....	78
Equilibrium diagram of water vapor, hydrogen, iron, and iron oxides, figure showing.....	46	I.	
Eutectic point of lime-silica system, figure showing.....	17	Illinois, coal from, ash analyses of.....	28
		Indiana, coal from, ash analysis of.....	27
F.		Initial deformation of cones, definition of.....	112
Feild, A. L., cited.....	19	values for.....	82
Ferric oxide, dissociation temperature of.....	20	Intumescence of ash cones, causes of.....	86
Fieldner, A. C., cited.....	29, 32	Iron, equilibrium of, with hydrogen and water vapor.....	45
		in ash, effect of reducing atmospheres on.....	116
		in fused ash and in clinker, state of.....	64, 117
		Iron oxides, in ash, effect on fusibility.....	20, 73
		reduction of.....	110
		J.	
		Jellico bed, Tenn., coal from, ash analyses of..	27, 28

## K.

	Page.
Kaolinite, melting point of .....	15
Kanolt, C. W., cited .....	16
Kansas, coal from, ash analysis of .....	28
Kreisinger, Henry, cited .....	110
on oxygen in fuel bed of coal fires .....	53

## L.

Le Chatelier, Henry, determination of fusing temperature of ash by .....	3
Lime, melting point of .....	16
in ash, percentage of .....	25
Lime-silica system, concentration-temperature diagram for, figure showing...	17
eutectic point of, figure showing .....	17
Lower Kittanning, Miller, or B bed, Pa., coal from, ash analyses of .....	28
Lower Weir-Pittsburg bed, Kans., coal from, ash analyses of .....	28

## M.

Magnesia, melting point of .....	16
percentage of in ash .....	25
Magnetism of fused ash cones .....	73
method of determining .....	95
Magnetite, melting point of .....	16
Marks, L. S., cited .....	1, 88
determination of fusibility of ash by .....	6
on differences in softening temperatures of ash .....	37
on position of ash cones in fusibility tests .....	79
on use of Seger cones .....	5
Mary Lee bed, Ala., coal from, ash analysis of .....	27
Maryland, coal from, ash analysis of .....	27
Mathesius, Ludwig, cited .....	64
Meker furnace, figure showing .....	22, 97
results of softening temperature tests in .....	32, 98
Melter's furnace, advantages of for softening tests .....	111
atmosphere in, analyses of .....	93, 94
description of .....	90
figure showing .....	91
results of tests in .....	96, 98, 104, 107
Melting interval, determination of .....	18
Michigan, coal from, ash analysis of .....	28
Miller or "B" bed, Pa., coal from, ash analyses of .....	28
Mingo bed, Tenn., coal from, ash analyses of .....	27
Molybdenum furnace, advantages of .....	89
ash cones from, appearance of .....	43
effect of hydrogen atmosphere in, figure showing .....	41
experiments with, description of .....	35
modified, description of .....	74
figure, showing .....	75, 76
view of .....	75
saturation for, description of .....	48
softening point tests in, results of .....	32, 33, 36
figure showing .....	41
view of .....	43
<i>See also</i> Furnace, molybdenum.	
Mueller, W. A., acknowledgment to .....	118

## N.

	Page.
Natural gas, analysis of .....	100
results of softening temperature tests with .....	98
figure showing .....	98
Nickel Plate bed, Ala., coal from, ash analysis of .....	27
No. 2 bed, Mich., coal from, ash analysis of .....	28
No. 5 bed, Ind., coal from, ash analysis of .....	27
No. 6 bed, Ill., coal from, ash analyses of .....	28
North Carolina, peat from, ash analysis of .....	28
North Dakota, lignite from, ash analysis of .....	28
Northrup furnace, ash cones from, appearance of .....	43
nature of reducing atmospheres in .....	39
result of softening point tests in, figure showing .....	40, 41
view of .....	42
<i>See also</i> Furnace.	

## O.

Oregon, coal from, ash analysis of .....	28
Osgood, F. D., acknowledgment to .....	118
Ovitz, F. K., cited .....	53
Oxides. <i>See</i> Iron oxides.	

## P.

Palmenberg, O. W., cited .....	88
on determination of fusibility of coal ash .....	11
on position of ash cone in fusibility tests .....	79
Pennsylvania, coal from, ash analyses of .....	27, 28
Peters, E. D., on fusibility of ferric oxide in ores .....	21
Pittsburgh bed, Md., coal from, ash analysis of .....	27
Pittsburgh bed, Pa., coal from, ash analyses of .....	28
Pittsburgh bed, W. Va., coal from, ash analyses of .....	27
Platinum furnace, ash cones from, appearance of .....	42
experiments with, description of .....	36
result of softening point tests in, figure showing .....	38, 41
<i>See also</i> Furnace.	
Pocahontas bed, W. Va., coal from, ash analyses of .....	28
Pocahontas No. 3 bed, Va., coal from, ash analyses of .....	27, 28
Preuler, G., cited .....	44
Prost, Eugene, determination of fusion temperature of ash by .....	2
Pyrite in coal, occurrence of .....	14
Pyrometer, optical, use of .....	31
Wanner, use of .....	32

## Q.

Quartz, melting point of .....	15
--------------------------------	----

## R.

Rankin, G. A., cited .....	17
Rate of heating, effect of, on softening temperature .....	115
Red Stone bed, W. Va., coal from, ash analysis of .....	27



	Page.		Page.
Reducing atmosphere, tests with.....	110	Softening temperatures in different furnaces, figure showing.....	38, 40, 41
effect of, on softening temperature of ash.....	116	in reducing atmospheres, figure showing.....	57
softening temperature of ash cones in.....	63	of Seger cones in reducing atmospheres and air.....	72
used in tests.....	49	in water vapor and hydrogen mix- tures, figure showing.....	51, 52
Reduction of iron oxide in ash, effect of.....	21	Sosman, R. B., on melting points of minerals.....	15
Ricketts, E. B., cited.....	79, 90	Spadra bed, Ark., coal from, ash analyses of.....	28
on determination of fusibility of coal ash.....	12	Stanton, S. M., cited.....	29
S.....		Steffe, Herman., cited.....	21
Saginaw bed, Mich., coal from, ash analysis of.....	28	Sterling bed, Tenn., coal from, ash analyses of.....	26
Saturator for hydrogen and water vapor mixtures, description of.....	48	Swelling of ash cones, causes of.....	86
figure showing.....	47		
for modified molybdenum furnace, de- scription of.....	78	T.....	
figure showing.....	76	Taylor, G. G., acknowledgment to.....	118
Seger cones, experiments with, description of.....	22-43	Temperature, maximum limit of, in com- mercial tests of ash.....	113
preparation of.....	29	See also Ash cones, fusing temperature, softening temperature.	
sizes of, used in test.....	30	Temperature measurements, methods of making.....	30, 49, 95
softening temperatures of.....	72	Tennessee, coal from, ash analyses of.....	27, 28
use of, by Hubley.....	9	Thermocouple, for standard softening-tem- perature tests, description of.....	113
by Le Chatelier.....	3	use of in softening-point tests.....	31, 96
by Marks.....	5, 7, 8	Texas, coal from, ash analyses of.....	28
by New York Edison Co.....	12	Thompson bed, Ala., coal from, ash analyses of.....	27
by Palmenberg.....	11		
to determine softening temperature.....	19	U.....	
See also Ash cones, cones.		Upper and Lower Banner bed, Va., coal from, ash analyses of.....	28
Sewell bed, W. Va., coal from, ash analyses of.....	28	Utah, coal from, ash analyses of.....	28
low ash content of.....	14		
Selvig, W. A., acknowledgment to.....	118	V.....	
Shepard, E. S., cited.....	19	Virginia, coal from, ash analyses of.....	27
Silica in ash of fuels tested.....	25	Viscosity of fused ash, effect of, on rate of de- formation of cones.....	52
in coal, occurrence of.....	14		
Silica-tube furnace, figure showing.....	46, 47	W.....	
See also Heraeus furnace.		Wanner pyrometer, use of, in tests.....	49
Silicates, ferrous and ferro-calcic, formation temperatures of.....	21	See also Pyrometer.	
Sillimanite in fuel-bed clinker.....	66	Washington, coal from, ash analyses of.....	28
Slags. See Clinker slags.		Water vapor, equilibrium of, with iron and iron oxides.....	44
"Softening interval," definition of.....	109, 113	West Virginia, coal from, ash analyses of.....	27, 28
Softening point, definition of.....	50, 81	Widow Kennedy bed, Va., coal from, ash analyses of.....	28
of ash cones, figure showing.....	34, 35	Wright, F. E., cited.....	17
Softening temperature, definition of.....	112	Wyoming, coal from, ash analyses of.....	28
determination of.....	30		
factors influencing.....	20		
of ash cones, effect of position on.....	80		
in reducing atmospheres.....	63		
of ash containing $\text{Fe}_2\text{O}_3$ .....	68		
figure showing.....	70, 71		
relation of, to temperature of complete melting.....	19		
tests, standard, crucibles for, description of.....	116		













